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# INTERNATIONAL TEMPERATURE SCALE AND SOME RELATED PHYSICAL CONSTANTS

By H. T. Wensel

ABSTRACT

The situation in regard to the radiation constants is reviewed primarily for the purpose of selecting the value of $c_2$ to use in Planck's equation for securing, above 1063° C, a temperature scale which most nearly conforms with the thermodynamic scale. The values in the literature are discussed, and some data are presented for deriving $c_2$ from gas thermometry data. The constants arrived at are the following:

$\sigma = (5.70 \pm 0.02) \times 10^{-5}$ erg sec $^{-1}$ cm$^{-2}$ deg $^{-4}$
$c_1 = (3.732 \pm 0.006) \times 10^{-5}$ erg cm$^2$ sec$^{-1}$
$c_2 = 1.436 \pm 0.001$ cm deg
$\lambda_m T = (2892 \pm 2) \times 10^{-4}$ cm deg
$M$ = least mechanical equivalent of light = $0.00151 \pm 0.00001$ watt ("new" lumen)$^{-1}$

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## I. INTERNATIONAL TEMPERATURE SCALE

In 1927 the Seventh General Conference of Weights and Measures, representing 31 nations, unanimously adopted the International Temperature Scale [1].[1] If the ratio of any two temperatures be defined by the equation $T_2/T_1 = 1 - E$, where $E$ is the efficiency of a completely reversible heat engine operating between a source at temperature $T_1$ and a sink at temperature $T_2$, and if further the temperature interval between the steam point and the ice point be defined as 100°, the resultant scale is the thermodynamic scale advocated by Lord Kelvin. Temperatures on this scale, known as the Kelvin Scale, are designated as "°K" and denoted by the symbol $T$. The lower limit of temperature is 0°K, and the normal freezing point of water, called the ice point and designated by the symbol $T_0$, is found by experiment to be approximately 273° K.

[1] Numbers in brackets indicate the literature references at the end of this paper.

The Kelvin Scale and other scales on which numerical values of temperature are a linear function of $T$ are the only thermodynamic scales which have been used to any considerable extent. If we write $t=T-T_0$, $t$ is the temperature on a scale which is called the Thermodynamic Centigrade Scale. Any temperature *interval* has the same numerical value when expressed on this scale as when expressed on the Kelvin Scale. The International Temperature Scale "conforms with the thermodynamic [centigrade] scale as closely as is possible with present knowledge" and "is to be regarded as susceptible of revision and amendment as improved and more accurate methods of measurement are evolved."

The possibility of revising the scale to secure some improvement appeared soon after the scale was adopted. Below 660° C the scale is defined by the standard resistance thermometer and from 660° C to the gold point, defined as 1063.0° C, the scale is defined by the standard thermocouple. The standard thermocouple and the standard resistance thermometer are made to agree at the freezing point of antimony, 630.5° C, but agreement at 660° C was left to chance. In 1929 Roeser [2] found that the agreement was within 0.01° C at the melting point of the sample of aluminum, 659.23° C, at which he compared thermocouples and resistance thermometers. Roeser used two thermocouples and obtained agreement to 0.01° C with one and 0.00° C with the other. It subsequently developed [3], however, that the silver used in this work had a freezing point 0.48° C lower than that of pure silver, corresponding to a difference of 5.5 microvolts in the electromotive force yielded by Roeser's thermocouples at the silver point. Making this correction, it is found that these thermocouples indicate the freezing point of the aluminum used to be 659.05° C, whereas the standard resistance thermometer indicated the temperature to be 659.23° C. Inasmuch as the standard thermocouple defines the scale only from 660° to 1063° C, the temperature in question is 659.23° C (Int. 1927), because it is in the range of the scale defined by the standard thermometer. Subsequently, the freezing point of a lot of aluminum to be used for standard samples was measured [2] with a standard resistance thermometer as 660.01° C and with a standard thermocouple as 695.87° C. The temperature in question is above the range defined in terms of the resistance thermometer and below the range defined in terms of the thermocouple and therefore cannot be expressed on the International Temperature Scale of 1927. This situation can be remedied by limiting the range of the scale defined by the resistance thermometer to temperatures below the freezing point of antimony and extending the range of the thermocouple down to that point.

Above the melting point of gold, the scale might well be based on the Planck formula instead of the Wien formula, which was used in defining the 1927 scale [1] up to about 5000° C, where $\lambda\,(t+273)$ is less than 0.3 cm deg. The use of the Planck formula would make no significant change in the scale below 5000° C and would result in a scale which conforms closely to the thermodynamic scale at all temperatures above the gold point.

A study of the question of whether other revisions might secure still closer conformity has led, among other things, to a re-evaluation of the

[2] The resistance thermometer measurements were made by R. S. Jessup and the thermocouple measurements by A. I. Dahl.

radiation constant which is used in defining the scale at high temperatures. A true perspective of the data on the radiation constants cannot be obtained without consideration of a number of other physical constants more or less directly related to the radiation constants. The numerical values of some of these related constants have been established so accurately that, in combining them with other constants which are much less accurately established, they may be treated as exact. Nevertheless, it seemed worth while to discuss all the constants involved in some detail, either to indicate how little the value selected contributes to the uncertainty of the derived radiation constants or to make the incidental results of this study available to readers who may find them of interest.

## II. THE RADIATION CONSTANTS

The constants by means of which the energy radiated by a black body may be characterized are $c_1$, $c_2$, $\sigma$, $\lambda_m T$, and $\nu_m/T$ defined by the formulas

$$J_\lambda = c_1 \lambda^{-5} \left( e^{\frac{c_2}{\lambda T}} - 1 \right)^{-1} \tag{1}$$

$$J_\nu = c_1 c^{-4} \nu^3 \left( e^{\frac{c_2 \nu}{T}} - 1 \right)^{-1} \tag{2}$$

$$\int_0^\infty J_\lambda d\lambda = \int_0^\infty J_\nu d\nu = \sigma T^4 \tag{3}$$

$$\lambda_m T = \frac{c_2}{A} = 0.201405 c_2, \tag{4}$$

where

$$A = 5(1 - e^{-A}) \tag{5}$$

and

$$\frac{\nu_m}{T} = \frac{Bc}{c_2} = 2.82144 \frac{c}{c_2}, \tag{6}$$

where

$$B = 3(1 - e^{-B}) \tag{7}$$

In the above formulas

$\lambda$ is the wavelength

$\nu$ is the frequency

$c$ $(= \lambda\nu)$ is the velocity of light

$T$ is temperature in degrees K

$e$ is the Naperian base, 2.7182818 . . .

$J_\lambda$ is the radiant energy (of wavelength $\lambda$) per unit wavelength interval emitted per unit time by unit area of a black body throughout the solid angle $2\pi$, i. e., "hemispherical radiation."

$J_\nu$ is the radiant energy (of frequency $\nu$) per unit frequency interval emitted per unit time by unit area of a black body throughout the solid angle $2\pi$.

$\lambda_m$ and $\nu_m$ are the values of $\lambda$ and $\nu$ at which $J_\lambda$ and $J_\nu$, respectively, are a maximum for any given value of $T$.

It should be pointed out that, for a given value of $T$, $\lambda_m$ and $\nu_m$ do not correspond to the same region of the spectrum. In other words,

their product is not $c$ but $c(B/A)$, or 0.56825 $c$, so that $\nu_m$ is displaced toward the red end of the spectrum from the value of $\nu$ corresponding to $\lambda_m$. This may be seen by writing $d\nu = -(c/\lambda^2)d\lambda$.

All magnitudes will be expressed in cgs units, i. e., $\lambda$ in cm, $J_\lambda$ in erg $sec^{-1}cm^{-3}$, $c_1$ in erg $sec^{-1}cm^2$, $c_2$ in cm deg, $\sigma$ in erg $sec^{-1}cm^{-2}deg^{-4}$, etc. In giving numerical values, factors of $10^n$ and the cumbersome designation of units such as those above will often be omitted after the first writing when it is felt that no ambiguity will result.

We have the following relations

$$c_1 = 2\pi c^2 h = \frac{15}{\pi^4}\sigma c_2^4, \tag{8}$$

$$c_2 = \frac{ch}{k} = \left(\frac{h}{e}\right)\frac{cF}{R}, \text{ and} \tag{9}$$

$$\sigma = \frac{2\pi^5 c^2 h}{15 c_2^4} = 40.8026\frac{c^2 h}{c_2^4}, \tag{10}$$

where $c$ = the velocity of light in cm $sec^{-1}$
$h$ = Planck's constant of action in erg sec
$k$ = the Boltzmann constant in erg $deg^{-1}$
$e$ = electronic charge in electrostatic units (esu)
$F$ = the faraday constant in (esu) $mole^{-1}$
$R$ = the gas constant in erg $deg^{-1}$ $mole^{-1}$.

There are a number of reviews available on the best values of the physical constants derivable from experimental data, but the radiation constants have not received much attention in recent years. The experimental values of $\sigma$ and $c_2$ have usually been used to calculate values of $h$, but not much weight has been given to the results. Better values of the radiation constants can be derived from atomic constants than from the published experimental values, and it seems worth while to make a critical study of these related constants for the primary purpose of deducing the most probable value of the constants which appear in the formulas for black-body radiation.

For practical work, a knowledge of the numerical value of any radiation constant, excepting $c_2$, to better than 1 or 2 percent is seldom required. Measurements involving $J_\lambda$ are usually so made as to depend only on *ratios* in which $c_1$ cancels out. Even when this is not the case, an accurate value of $c_1$ is seldom of interest, because we have at present no technique for accurate measurements of $J_\lambda$. The situation in regard to $\sigma$ is substantially the same. The only experiments in which anything besides an approximate value of $\sigma$ is of interest are those made for the purpose of determining $\sigma$.

Our interest in the constant $c_2$ lies in the fact that it is one of the constants used in defining the International Temperature Scale above the melting point of gold. This definition is "by means of the formula

$$\log_e \frac{J_2}{J_1} = \frac{c_2}{\lambda}\left(\frac{1}{1336} - \frac{1}{(t+273)}\right) \tag{11}$$

The constant $c_2$ is taken as 1.432 cm degrees. The equation is valid if $\lambda(t+273)$ is less than 0.3 cm degrees." In this equation $J_1$ and $J_2$ are the values of $J_\lambda$ at the melting point of gold, defined as 1063°, and at the temperature $t$, respectively. A change in $c_2$ of 1 percent results

in a change in $t$ of more than 10° at the melting point of platinum and of more than 60° at the melting point of tungsten.

## III. AUXILIARY CONSTANTS

In giving the numerical value of a quantity it is usually advisable to add a numerical statement of the uncertainty associated with the value given. The ± terms in this paper represent the limits within which it is estimated that the true value is included with a probability of about 0.9. They represent merely the author's opinion and may bear little relation to the mean deviation.

### 1. VELOCITY OF LIGHT

The velocity of light is so accurately known that, for the calculations made in this paper, it may be treated as exact. Karolus and Mittlestaedt [4] obtained the value $2.99778\times10^{10}$, while (Michelson), Pease, and Pearson [5] obtained the value $2.99774\times10^{10}$. The velocity of light is taken as

$$c=(2.99776\pm0.00020)\times10^{10}\ \text{cm sec}^{-1}.$$

### 2. KELVIN TEMPERATURE OF THE ICE POINT AND THE VALUE OF $R$

The temperature of the ice point on the Kelvin Scale, $T_0$, has been derived in a number of laboratories. The most recent and reliable of the values are listed in table 1.

TABLE 1.—*Recent values of* $T_0$

| Authors | Laboratory | Date | $T_0$ |
|---|---|---|---|
| Heuse and Otto [6] | PTR | 1930 | 273.16 |
| Keesom and Tuyn [7] | Leiden | 1936 | 273.14 |
| Roebuck [8] | University of Wisconsin | 1936 | 273.16 |
| Kinoshita and Oishi [9] | Tokyo University | 1937 | 273.167 |
| Beattie [10] | MIT | 1937 | 273.16–273.17 |
| | | Mean | 273.16 |

The value 273.16 to 273.17 listed for Beattie is provisional as Beattie's final calculations have not been completed. On the basis of the determinations listed in table 1,

$$T_0=273.16\pm0.02°\text{K}.$$

The value of $RT_0$ needs little comment as it is known more accurately than $T_0$. The value for $RT_0$ given by Birge [11] reduces to $2.2711\times10^{10}$ erg mole$^{-1}$. Combining this with $T_0=273.16$, the value of $R$ is found to be

$$R=(8.3142\pm0.0010)\times10^{7}\ \text{erg deg}^{-1}\ \text{mole}^{-1}.$$

### 3. INTERNATIONAL ELECTRICAL UNITS

Many of the experimental data to be considered are expressed in International Electrical Units. In order to reduce the published

results to electrostatic units (esu) for substitution in eq 9 the ratios of the international to the absolute units must be used. The most recent published determinations of the ratios of the international to the absolute (practical) units are summarized on page 113 of the Procès Verbaux des Seances, Comité International des Poids et Mesures of 1937. Inasmuch as this publication is not generally available the summary is reproduced below:

| | | |
|---|---|---|
| ETL (Japan) | 1 international ohm | $=1.00046_5$ abs. ohms. |
| NBS (U. S.) | 1 international ohm | $=1.00045_4$ abs. ohms. |
| NPL (Great Britain) | 1 international ohm | $=1.00050_4$ abs. ohms. |
| PTR (Germany) | 1 international ohm | $=1.00048_3$ abs. ohms. |
| ETL | 1 international ampere | $=0.99993_8$ abs. ampere. |
| NBS | 1 international ampere | $=0.99989_5$ abs. ampere. |
| NPL | 1 international ampere | $=0.99984_8$ abs. ampere. |
| ETL | 1 international volt | $=1.000403$ abs. volts. |
| NBS | 1 international volt | $=1.000349$ abs. volts. |
| NPL | 1 international volt | $=1.000352$ abs. volts. |

The most recent NBS value [12] for the ampere, however, is 0.99986, which is in remarkably good agreement with the NPL value. From these data the following values have been derived:

$$\frac{\text{1 International Ohm}}{\text{1 Absolute Ohm}}=p=1.00048.$$

$$\frac{\text{1 International Ampere}}{\text{1 Absolute Ampere}}=q=0.99986.$$

$$\frac{\text{1 International Volt}}{\text{1 Absolute Volt}}=pq=1.00034.$$

### 4. THE FARADAY

In 1929 Birge [11] recommended 96,487 abs. coul. for the faraday and is still using this value, since his latest value [13] of 96,513.1 abs. coul. per mole on *the physical scale* (atomic weight of oxygen = 1.00027 $\times 16$) is simply 1.00027 times his 1929 value. This value is based entirely on the determinations of $F$ with the silver voltameter. It is the proper value to use in equations connecting atomic constants (as Birge himself points out) only if the measured amount of silver deposited in a silver voltameter by the passage of a given charge of electricity truly represents the mass associated with that amount of charge. There is reason to believe that this is not the case. While it is true that the difference is of no consequence in deriving values of the radiation constants, it cannot be ignored if one wishes to express the faraday to 0.1 coul.

In the first place, on account of inclusions and similar causes, the mass *deposited* by one coulomb is not the mass of silver ions with which one coulomb of charge is associated. Correction is usually made for inclusions, but there may be other effects which are not known. In the second place, the amount of silver *deposited* is not necessarily the amount of silver *weighed*. It may be worth while to quote a few sentences from a discussion of this question by Rosa and Vinal [14]. "The precaution taken by some observers to soak the silver deposits over night in distilled water to remove the last traces

of electrolyte was shown to be harmful because it was discovered that silver in contact with platinum is appreciably soluble in distilled water. This was shown by repeated tests. The silver and the platinum differ slightly in potential so that a current passes from the silver to the platinum through the water." If acid is present in the electrolyte there will, of course, be a re-solution of the deposit. Although there is no difficulty in avoiding loss of deposit due to acidity of the electrolyte, the question of re-solution in a neutral electrolyte still remains, inasmuch as in the usual form of silver voltameter, the silver is deposited on platinum.

All of these effects, as long as they are constant, have no bearing on the use of the silver voltameter as a device for reproducing the international ampere defined as the current which will deposit 0.001118 g of silver per second in a silver voltameter. The technique of the silver voltameter has been so well worked out that it is a precision device capable of being used to check the voltage of the Weston normal cell. Rosa and Vinal [14] list six determinations of this voltage in five different countries with an average deviation of 1 part in $10^5$ from the mean and a *maximum* deviation of less than 2 parts in $10^5$.

The international ampere, so defined, is thus transferred to standard cells and material resistance standards (wire coils) which are then used to reproduce the international ampere in the various national laboratories. There are small differences in these material standards but they amount to only a few parts in $10^5$ and can be neglected. We have then, from the silver experiments, that

$$F=\frac{\text{at. wt. of Ag}}{0.001118}=\frac{107.880}{0.001118}=96{,}494 \text{ int. coul. mole}^{-1}.$$

While the statement "in a silver voltameter a weighed deposit of 1 mole will result from the passage of 96494 int. coul." is true to about 1 part in $10^5$, the uncertainty in the above figure as a value of $F$ is determined by the magnitude of the effects described earlier. We will not question the fact, which must be true if values of the specific electronic charge, $e/m$, are to be deduced from $F$, that each univalent ion carries the charge $e$.

It is evident, then, that the definition of the international ampere in terms of the silver voltameter does not confer any special virtue on silver in the determination of the faraday. In fact, if we used a different element which was free from all effects of the kind described, it would yield a more reliable value of $F$. Unfortunately, there are very few elements that are suitable. There must be no question of the valence. If we have, for example, both univalent and divalent ions, the result will be entirely useless. Iodine is one of the few that can be used. It is free from the effect of inclusions, but the mass determined by titration may differ from the mass deposited due to oxidation by the arsenious acid solution used in the titration. The value of the faraday obtained with the iodine voltameter is 96,514 int. coul. per g equiv. [15]. There seems no logic, whatever, in ignoring the iodine value. The effects in the two cases are not known, but it seems fairly certain that the faraday lies somewhere between the two values whose mean is 96,504 int. coul. There is no point in weighting the silver value higher than the other simply because more work has been done with the silver voltameter. This difference of 20 parts

per $10^5$ is inherent in the two methods and would probably not be greatly changed by more determinations.

To get $F$ in units which can be used by atomic physicists we must know the relation between the absolute and international ampere. For this we now have a reliable conversion factor $q$. The various determinations yield the ratio of the size of the absolute ampere to the international ampere as represented in each case by the material standards, standard cells and standard resistance coils, at the national laboratory making the determination. The differences in these material standards can be neglected and well within the accuracy with which we can at present evaluate the faraday, the conversion factors apply to the international ampere as defined in terms of the silver voltameter, that is, to the value of $F=96{,}504$.

In 1906–07 an extended investigation was carried out at the National Physical Laboratory [16] in which the silver deposited by one absolute coulomb in the "New Form" of silver voltameter was $0.00111815_1$. The absolute ampere was realized with the Ayrton-Jones current balance. This is not a determination of $F$, but a determination of

$$q=\frac{0.0011180}{0.00111815_1}=0.99986.$$

This value, while not comparable in accuracy with recent determinations, agrees surprisingly well with the best of these.

The value of the faraday is then 96,504 int. coul. $mole^{-1}$, or 96,490 abs. coul. $mole^{-1}$. This value does not differ much from the one Birge is now using but is based on different data. His use of only the silver data was to a large extent balanced by his use of an obsolete value of $q$.

Expressing the result in electrostatic units

$$\boldsymbol{F=(2.8926\ \pm 0.0002)\times 10^{14}\ (\text{esu})\ \text{mole}^{-1}}$$

### 5. VALUES OF $e$ AND $h$

For the purposes of this paper an accurate value of the ratio $h/e$ is of far more concern than accurate values of either $h$ or $e$. There is some divergence in the fourth significant figure of the value advocated for $e$. It appears that the value derived by Von Friesen [17] is based upon impartial consideration of the data available. This value is

$$\boldsymbol{e=(4.800\ \pm 0.005)\times 10^{-10}\ (\text{esu})}$$

The value of $e=4.800$ and the value of $h/e$ listed on page 392 lead to a value of

$$\boldsymbol{h=(6.61\ \pm 0.01)\times 10^{-27}\ \text{erg sec.}}$$

This value agrees to three significant figures with all the recent values, see table 5.

## IV. VALUES OF $c_2$ FROM $\lambda_m T$.

One of the most direct methods of evaluating $c_2$ is by the use of eq 4. The published results are listed in table 2.

TABLE 2.—*Values of $c_2$ from measurements of $\lambda_m T$*

| Authors | Year | Published values | Selected values |
|---|---|---|---|
| Lummer and Pringsheim [18] | 1899<br>1901 | 1.43 and 1.46<br>1.458 | 1.45 |
| Paschen and Wanner [19] | 1899<br>1900<br>1901 | 1.435<br>1.441<br>1.447 | 1.44 |
| Holborn and Valentiner [20] | 1907<br>1912 | 1.42<br>1.435 | 1.435 |
| Warburg, Leithauser, Hupka, and Müller [21] | 1910<br>1911<br>1912<br>1913<br>1915 | 1.457<br>1.42 to 1.46<br>1.436 and 1.438<br>1.4374<br>1.425 and 1.43 to 1.44 | 1.43 |
| Coblentz [22] | 1914<br>1916<br>1922 | 1.4465<br>1.4369<br>1.4318 | 1.432 |
| Mendenhall [23] | 1914<br>1917 | 1.44<br>1.4394 | 1.439 |
| Michel [24] | 1922 | 1.427 | 1.427 |
| Unweighted mean<br>Mean deviation | | | 1.4361<br>0.0059 |

All the values listed in the third column except those of Coblentz and of Holborn and Valentiner represent separate determinations. Holborn and Valentiner's value of 1.435 is merely a correction by Valentiner of the value originally reported as 1.42. Coblentz's values of 1916 and 1922 represent only corrections of the value originally published in 1914.

It is evident that a mean of all the published values would have little or no significance. The best value derivable from these data would be a weighted mean of the selected values, but it is very difficult to assign weights to such observations. These selected values are the final values arrived at by the various groups of experimenters. In cases where reported values of $c_2$ were based on the equation $c_2=5\lambda_m T$ obtained by using Wien's formula instead of eq 4, the values have been recalculated.

## V. VALUES OF $c_2$ FROM $\sigma$

The second method for obtaining $c_2$ is from measurements of $\sigma$ as defined by eq 3 and the relation given in eq 8. Substitution of the numerical values of $c$ and $h$ from section III in the latter yields the relation

$$c_2=0.12477\sigma^{-1/4} \tag{12}$$

In table 3 are listed the available data on $\sigma$ with values of $c_2$ calculated from eq 12.

TABLE 3.—*Experimental values of $\sigma$ and corresponding values of $c_2$*

| Authors | Year | Reported values of $\sigma 10^5$ | Selected values of $\sigma 10^5$ | $c_2=0.12477\,\sigma^{-1/4}$ |
|---|---|---|---|---|
| Lehnebach [25] | 1874 | 4.58 | | |
| Kundt and Warburg [26] | 1878 | 4.62 | | |
| Graetz [27] | 1880 | 4.5 | | |
| Christiansen [28] | 1883 | 5.04 | | |
| Scheiner [29] | 1909 | 4.8 | | |
| Kurlbaum [30] | 1898 | 5.33 | 5.33 | 1.460 |
| Féry and Drecq [31] | 1909 | 6.30 | 5.89 | 1.424 |
| | 1911 | 6.51 | | |
| | 1912–13 | 5.57 and 6.20. | | |
| Todd [32] | 1909 | 5.48 | 5.48 | 1.439 |
| Bauer and Moulin [33] | 1909 | 6.0 | 5.3 | 1.462 |
| | 1910 | 5.3 | | |
| Valentiner [34] | 1910 | 5.36 | 5.58 | 1.447 |
| | 1912 | 5.58 | | |
| Shakespear [35] | 1912 | 5.67 | 5.67 | 1.438 |
| Puccianti [36] | 1912 | 5.96 | 5.96 | 1.429 |
| Westphal [37] | 1912–13 | 5.57 | 5.57 | 1.444 |
| Gerlach [38] | 1912 | 5.803 | 5.80 | 1.430 |
| | 1916 | 5.85 | | |
| | 1920 | 5.80 | | |
| Keene [39] | 1913 | 5.89 | 5.89 | 1.424 |
| Coblentz [40] | 1914 | 5.6 | 5.72 | 1.433 |
| | 1916 | 5.72 | | |
| Foote [41] | 1918 | 5.7 | 5.7 | 1.426 |
| Kahanowicz [42] | 1919 | 5.61 | 5.61 | 1.442 |
| Wachsmuth [43] | 1921 | 5.723 | 5.723 | 1.435 |
| Müller and Császár [44] | 1923 | 5.72 | 5.72 | 1.433 |
| Hoffmann [45] | 1923 | 5.764 | 5.764 | 1.432 |
| Kussmann [46] | 1924 | 5.795 | 5.795 | 1.430 |
| Hoare [47] | 1928 | 5.735 | 5.735 | 1.434 |
| Müller [48] | 1928 | 5.771 | 5.771 | 1.432 |
| Mendenhall [49] | 1929 | 5.79 | 5.79 | 1.430 |
| Mean | | | 5.69 | 1.4368 |
| Mean deviation | | | 0.13 | 0.0087 |

There is considerable uncertainty in these values arising from the corrections of about 2 percent which are usually made for the lack of blackness of the receiver. The values reported by Hoare and by Mendenhall are the only ones which do not involve any uncertainty from such corrections and are considered the most reliable. Many of the values originally reported have been corrected in later publications, but the original values are used except in cases where the corrections were made by the men who originally reported the results. Thus Valentiner corrected his value of 5.36 to 5.58 and Kurlbaum's value of 5.33 to 5.45. Valentiner's corrected and Kurlbaum's original values are selected for use in obtaining the mean. The first five values reported have been included in the table merely because of their historical interest.

A weighted mean of the values in table 3 would probably yield a better value than the one derived, but the assigning of such weights is not attempted. It is evident that in general the earlier values of $\sigma$ are smaller and the derived value of $c_2$ larger than the later ones. Thus the first 10 values of $c_2$ listed in table 3 have a mean of 1.439,

and the last 10 have a mean of 1.434. On the assumption that the later values are more reliable, they might be given more weight, but this assumption is open to some question. It is felt that there are enough values to minimize the effect of including a few which are believed to be somewhat less reliable than the others and the unweighted mean seems the wiser choice.

## VI. VALUES OF $c_2$ BASED ON OPTICAL-PYROMETER MEASUREMENTS

Another method which was used by Mendenhall [23] and by Day and Sosman [50] has not been given much attention because of the scarcity of the required experimental data. Equation 11, defining the International Temperature Scale of 1927, may be written

$$c_2=\lambda \ln \frac{J_t}{J_{Au}} \frac{(t+273)(t_{Au}+273)}{t-t_{Au}}=\lambda \ln \frac{J_t}{J_{Au}} f(t) \tag{13}$$

The product $\lambda \ln J_t/J_{Au}$ may be measured with an optical pyrometer and $c_2$ calculated for any case where the corresponding temperatures are known on the thermodynamic scale.

Day and Sosman and Holborn and Day [51] have measured the temperature of a large number of fixed points on the constant-volume nitrogen gas scale with a pressure at 0° C. of approximately 300 mm of mercury. The corrections to convert [52] these temperatures to the Centigrade Thermodynamic Scale are only a fraction of a degree even at the palladium point. Some of these temperatures, so corrected, are given in table 4. Day and Sosman did not make measurements at the copper-silver eutectic point, but their scale was so well described in terms of other fixed points, that temperatures in this region can be determined on their scale with considerable precision. Mendenhall and Forsythe [53] have determined the ratio of the temperatures of the gold and palladium points on the Kelvin Scale by means of eq 3. They found that the energy radiated by a black body at the palladium point was 3.4626 times that radiated by a black body at the gold point. From this

$$\frac{t+273}{1336}=\sqrt[4]{3.4626}, \text{ or } t=1549.5° \text{ C}.$$

The value of $\lambda \ln J_t/J_{Au}$ for palladium listed in table 4 is that of Fairchild, Hoover, and Peters [54]. These authors compared their palladium with samples used by Day and Sosman and found the melting point to be the same within 0.1° C. The value for the nickel point is that of Wensel and Roeser [55] and the remaining values represent unpublished work by these same experimenters.

In the case of copper, the size of the interval, about 20° C, precludes the determination of $c_2$ to better than about 1 percent. Although Day and Sosman ascribe an uncertainty of about ¾° to each of the gold and silver points, the nature of their measurements was such that the systematic or constant errors in their work would have the same sign and be of about the same magnitude at these two points. The difference between them is probably good to ±0.2° C, in the same

way that the interval between gold and copper is certainly not in error by more than 0.2°. At the copper-silver eutectic point the uncertainty in $c_2$ is caused largely by the inability to make highly accurate optical-pyrometer measurements at the comparatively low brightness level corresponding to that temperature.

TABLE 4.—*Values of $c_2$ based on optical pyrometry*

| Fixed points | Temperature | Authors | Method | $f(t)$ | $\left(\lambda \ln \frac{J_t}{J_{Au}}\right) \times 10^7$ | $c_2$ |
|---|---|---|---|---|---|---|
| | °C | | | | | |
| Pd | 1549.8 | Day and Sosman | Gas thermometer | 4997 | 2878 | 1.438 |
| Ni | 1453.0 | do | do | 5905 | 2430 | 1.435 |
| Cu | 1082.8 | do | do | 896×10³ | 159.5 | 1.429 |
| Au | 1062.6 | do | do | | | |
| Ag | 960.2 | do | do | −16085 | −891.5 | 1.434 |
| Cu-Ag | 778.2 | (Indirect) | do | −4937 | −1912 | 1.458 |
| Cu | 1084.3 | Holborn and Day | do | 903×10³ | 159.5 | 1.441 |
| Au | 1064.2 | do | do | | | |
| Ag | 961.7 | do | do | −16108 | −891.5 | 1.456 |
| Pd | 1549.5 | Mendenhall and Forsythe. | Radiation pyrometer | 5003 | 2878 | 1.440 |
| Au | 1063.0 | | (Used as base) | | | |
| Unweighted mean | | | | | | 1.4394 |
| Mean deviation | | | | | | 0.0029 |

## VII. VALUES OF $c_2$ FROM ATOMIC CONSTANTS

In view of the material presented in the preceding sections, the adoption in 1927 of $c_2=1.432$ cm deg in the definition of the International Temperature Scale seems to call for some explanation.

The values of $c_2$ derivable from experimental values of $\lambda_m T$ and from the gas-thermometer determination of the palladium point were essentially the same in 1927 as those given in this paper, namely, 1.436 and 1.438, respectively. The value of $c_2$ derivable from $\sigma$, however, was about ¼ percent lower than that derived today from the same value of $\sigma$, because the accepted value of $h$ was then about 6.55, or 1 percent, lower than that accepted today. A value of $h=6.55$ and $\sigma=5.7$ corresponds to a value of $c_2=1.432_8$. Moreover, the values of $h/e$ advocated in 1927 yielded values of 1.432 to 1.433. As the confidence placed in the available values of $h$ and $h/e$ at that time was such that they were generally expressed to four or five significant figures, the discrepancies in $c_2$ were not considered serious. The data on $\lambda_m T$ are not such as, in themselves, to inspire much confidence, and the value of $c_2$ deduced from the temperature of the palladium point was considered to indicate that Day and Sosman were overly optimistic in claiming an accuracy of 2° for their determination of this temperature. The history of the values of $h$ and of $h/e$, as outlined in table 5 and figure 1, explains the choice of the value of $c_2$ (shown by the star at 1927 in fig. 1) used in defining the temperature scale.

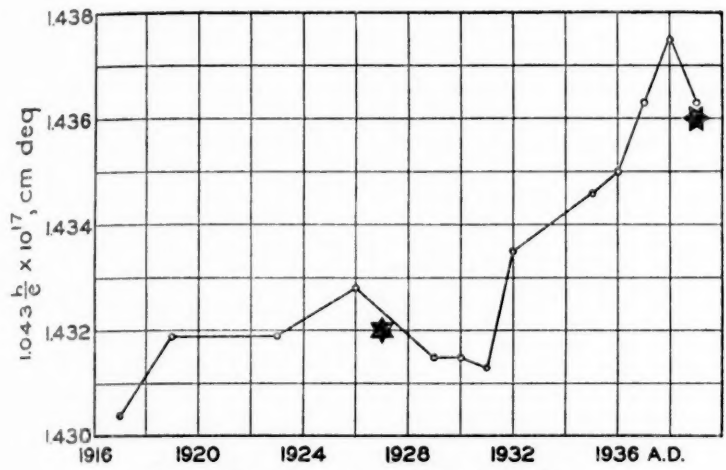


FIGURE 1.—*Values of $c_2$ calculated from h/e.*

TABLE 5.—*Values of h and of h/e which have been recommended by various reviewers*

| Year | Recommended by | $h\times10^{27}$ | $(h/e)\times10^{17}$ | 1.0430 $(h/e)\times10^{17}=c_2$ |
|---|---|---|---|---|
| 1917 | Millikan [56] | 6.547 | 1.3714 | 1.4304 |
| 1919 | Birge [57] | 6.550 | 1.3729 | 1.4319 |
| 1923 | Int. Crit. Tables [58] | 6.554 | 1.3729 | 1.4319 |
| 1926 | Birge [59] | 6.560 | 1.3737 | 1.4328 |
| 1927 | ITS [1] | | 1.373 | 1.432 |
| 1929 | Birge [11] | 6.547 | 1.3725 | 1.4315 |
| 1930 | Millikan [60] | 6.547 | 1.3725 | 1.4315 |
| 1931 | Bond [61] | 6.5586 | 1.3723 | 1.4313 |
| 1932 | Birge [62] | 6.5443 | 1.3744 | 1.4335 |
| 1935 | Beardon [63] | 6.558 | 1.3755 | 1.4346 |
| 1936 | Birge [64] | 6.58 and 6.61 | 1.37588 | 1.4350 |
| 1937 | Von Friesen [65] | 6.61 | 1.3771 | 1.4363 |
| 1938 | Millikan [66] | 6.61 | 1.3782 | 1.4375 |
| 1939 | Dunnington [67] | 6.6133 | 1.3771 | 1.4363 |

Since the values of $c$, $F$, and $R$ are all very accurately known, the quantity $cF/R=1.0430\times10^{17}$ may be taken as exact and eq 9 written as

$$c_2=1.0430\ h/e\times10^{17}. \tag{14}$$

The confidence which may be placed in this value of $cF/R$ is indicated by the fact that the constants in the oldest reference available in which all three are given, the 1897 edition of the Smithsonian Tables, yield 1.0429, those in the first (1910) volume of "Tables Annuelles de Constantes" yield 1.0428, while those recommended by Birge [11] in 1929 yield 1.0431. Using the constants in the ICT, the result is 1.0435. The value of $c_2$ calculated from formula 14 therefore, will be as accurate as the value used for $h/e$.

The reason for the sharp upturn in the accepted values of $h$ and $h/e$ about 1932 is to be found in a change in the views held in regard to the electronic charge, $e$. Up to 1928 no determination had been made since Millikan [68] obtained the value $4.774\times10^{-10}$ (esu) (later [60]

recalculated as 4.770) and the numerical value of $e$ was based entirely upon his result by the oil drop method. In 1928 Bäcklin [69] measured $e$ as 4.793 by an X-ray method, but his work made very little impression until confirmed by other workers both by X-ray and electron-diffraction methods. This led to a reexamination of Millikan's work, and a redetermination of the viscosity of air by Kellström [70] showed that this is about 1 part in 150 greater than the value used by Millikan in his original calculations. With this modification, Millikan's value is in agreement with values obtained by other methods as well as with a more recent [71] and accurate determination of 4.800 by the oil drop method. In the last 10 years there have appeared seven determinations [65] of $e$, ranging from 4.793 to 4.806, by three different methods, the average of which is $4.800\times10^{-10}$ (esu). This value is believed to be accurate to $\pm0.1$ percent.

The constant $h$ is never determined except in combination with $e$, the quantity actually determined being $Q=h/e^{n+1}$, where $n$ has the value 0, 1/3, or 2/3, depending on the type of experiment. The most accurate values of $Q$ are obtained in experiments of X-ray diffraction from calcite and from ruled gratings [3] yielding values of $h/e^{4/3}$ and $h/e^{5/3}$, respectively. We have then that

$$\frac{d(h/e)}{h/e}=n\frac{de}{e}+\frac{dQ}{Q}$$

so that, aside from the error in $Q$, the percentage error in $h/e$ is always less than that in $e$. The various determinations of $h/e^{n+1}$ have been carefully examined and the values of $h/e$ shown in table 6 have been derived on the following basis:

Calcite grating space$=3.0356\times10^{-8}$ [72]
$c=2.99776\times10^{10}$
$e=4.800\times10^{-10}$
1 International Volt$=1.00034$ Absolute Volts

TABLE 6.—*Experimental values of h/e*

| Authors | Year | Method | $(h/e)\times10^{17}$ |
|---|---|---|---|
| Lawrence [73] | 1926 | Ionization potentials | 1.3753 |
| Millikan [74] | 1916 | Photoelectric effect | 1.3777 |
| Lukirsky and Prilĕznev [75] | 1928 | do | 1.3711 |
| Olpin [76] | 1930 | do | 1.3748 |
| Wagner [77] | 1920 | X-rays | 1.3727 |
| Duane, Palmer, and Yeh [78] | 1921 | do | 1.3784 |
| Feder [79] | 1930 | do | 1.3757 |
| Kirkpatrick and Ross [80] | 1934 | do | 1.3752 |
| Schaffberger [81] | 1935 | do | 1.3766 |
| From Rydberg constant [82] | ..... | $e/m=5.2730\times10^{17}$ | 1.3787 |
| Gnan [83] | 1934 | Electron diffraction | 1.3765 |
| Von Friesen [84] | 1935 | do | 1.3769 |
| Eddington [85] | 1933 | $ch/2\pi e^2=137$ | 1.3783 |

[3] The latter method yields

$$\frac{h}{e^{4/3}m^{1/3}}=\frac{h}{e^{5/3}}\left(\frac{e}{m}\right)^{1/3},$$

but the value of $e/m$ is an independently determined constant, the measurement of which is not affected by $e$, and thus becomes part of the measurable quantity $Q$. In fact the measured value $e/m$, together with $e$, constitutes the determination of $h/e$.

There are many determinations from ionization potentials but, in most of these, accuracy beyond two significant figures was not even sought. Lawrence's result is the only one worth considering here. Lawrence's reported value of 1.3737 from the ionization potential of mercury vapor and the equation

$$Ve=\frac{hc}{\lambda}, \text{ or } \frac{h}{e}=\frac{V\lambda}{c} \tag{15}$$

was based on the international volt and $c=3\times10^{10}$. On the basis used here we get

$$h/e=1.00034\times\frac{3}{2.99776}\times1.3737=1.3753$$

Strictly speaking, this is in no sense a "correction" of Lawrence's result, but an expression of $h/e$ on a different basis. Lawrence's actual result is a value of 10.40 international volts for the limit of the mercury absorption spectrum $\lambda=1.188\times10^{-5}$. From this we have that

$$\frac{h}{e}=\frac{1.00034\times10.40\times10^{8}}{2.99776\times10^{10}}\times\frac{1.188\times10^{-5}}{2.99776\times10^{10}}=1.3753\times10^{-17}$$

This result is entirely independent of the value of $e$.

From measurements of the photoelectric effect, Millikan obtained a value of $h=6.57\times10^{-27}$ based on $c=3\times10^{10}$ and $e=4.774\times10^{-10}$. On our basis, therefore, his work yields

$$h/e=\frac{6.57}{4.774}\times\frac{3}{2.99776}\times1.00034=1.3777.$$

Lukirsky and Prilĕzaev obtained $h=6.543$ based on $e=4.774$. This result requires adjustment for $e$ and for reduction to the absolute volt, but not for $c$. Olpin obtained $h=6.541$, using sodium treated with sulfur vapor, and states in his prefatory abstract "An almost identical value is obtained for untreated sodium." However, in the body of the paper his result for untreated sodium is given as $h=6.6$, with the observation that it is not as reliable as the value 6.541. Von Friesen [65] in his table IV quotes Olpin's result as $h=6.561$, which is the mean obtained by giving the value 6.6 one-half as much weight as the value 6.541. This seems to be as good a way as any to treat Olpin's result, and from it we get

$$h/e=\frac{6.561}{4.774}\times1.00034=1.3748.$$

Determinations of $h/e$ by this method likewise do not require a knowledge of $e$.

The X-ray method also determines $h/e$ from eq 15, that is,

$$\frac{h}{e}=\frac{v\lambda}{c}=\frac{V\lambda}{c^2}\times10^{8}=\frac{2dV^{1}(1.00034)\sin\theta\times10^{8}}{c^2}, \tag{16}$$

where $v$ is in (esu) of potential difference, $V$ is in absolute volts, $V^1$ is in international volts, and $d$ is the grating space of calcite. The result does not depend on $e$ unless the value used for $d$ is made to

depend on $e$. In the past, $d$ has usually been calculated from the physical properties of calcite, using an equation in which $d$ is proportional to $\sqrt[3]{e}$. When $e$ was put equal to 4.770 or 4.774 a value of $d$ (about $3.028\times10^{-8}$) was obtained which required X-ray wavelengths found with crystal spectrometers to be multiplied by 1.00248 to make them agree with X-ray wavelengths measured with ruled gratings [72]. In other words, measurements by the two methods will agree if $d$ for calcite is taken as $1.0025\times3.028\times10^{-8}=3.0356\times10^{-8}$. If, on the other hand, we calculate $d$ on the basis of $e=4.800$, we get $d=3.028(4.800/4.770)^{1/3}=3.0344$. We get about the same values of $h/e$, therefore, from the crystal X-ray work by using the multiplying factor $(4.800/e)^{1/3}$ or by using Beardon's [72] value of $d=3.0356$, which is obtained by comparing ruled-grating measurements with crystal measurements of X-ray wavelengths. The latter method is more direct and will be used. The following values of $V^1 \sin\theta$ are available for calcite.

| | |
|---|---|
| Wagner | 2031.5 |
| Duane, Palmer, and Yeh | 2039.9 |
| Feder | 2036.0 |
| Kirkpatrick and Ross | 2035.3 |

Putting $d=3.0356$ and the above values of $V^1 \sin\theta$ into eq 16, we get the corresponding values of $h/e$ listed in table 6. Schaitberger, on the other hand, used a rock-salt crystal, taking $d=2.814$. He expressed his result as $h/e\alpha=1.3743$ on the basis of the absolute volt, $e=4.774$, and $c=2.99774$, where $\alpha$ is the factor which converts the conventional $d$ to true $d$. The simplest way to get $h/e$ from this is to put

$$\alpha=\sqrt[3]{\frac{4.800}{4.774}}=1.0018,$$

whence $h/e=1.3768$. Kirkpatrick and Ross have characterized Duane's result as too high and Wagner's as too low. They apply corrections to make the former 2034.6 but do not correct the latter. It seems advisable to take each result as reported, as it makes very little difference in the result sought here.

To get $h/e$ from the Rydberg number, $R_\infty$, we use the equation

$$\frac{h}{e}=\sqrt[3]{\frac{2\pi^2e^2}{R_\infty ce/m}} \tag{17}$$

The value of $R_\infty$ is 109737.4 [11], and, on the basis of the selected values of $e$ and $c$, $h/e$ is simply a question of the numerical value of $e/m$. However, Birge [82] has recently published a review of 10 determinations of $e/m$ and concludes that the best derivable value is $1.7591\times10^7$ (emu)$g^{-1}$, or $5.273\times10^{17}$ (esu)$g^{-1}$, on a basis substantially equivalent to the one used in this paper. Dunnington [67] arrives at the value $1.7590\times10^7$ (emu)$g^{-1}$. Inasmuch as the highest and the lowest of the 10 values listed by Birge yield values of $h/e$ differing by less 0.1 percent, it is evident that the value of $h/e$ from equation 17 is largely dependent on and not much more accurate than the value used for $e$. For this reason it should not be given as much weight as would be the case if a more accurate value of $e$ were available.

Gnan reported $h/e$ as 1.374, but points out that his result depends on the value of $e$. He then states that his explicit result is $h/e^{4/3}=1.758\times10^{-14}$, which is independent of his crystal constant. From this, $h/e=\sqrt[3]{.4800}\times1.758\times10^{-17}=1.3765\times10^{-17}$. Unfortunately, Von Friesen's Uppsala dissertation is not available to the writer, but Von Friesen [57] himself gives his result for $h$ as 6612/6610 of that of Gnan. From this we obtain $h/e=1.3769$ for Von Friesen's work.

Eddington's theoretical value of 1/137 for the fine structure constant is listed as a matter of interest. The mean obtained from the data listed in table 7, however, does not include this value, although, as a matter of fact, the mean is not appreciably changed if this value is included.

TABLE 7.—*Summary of values of h/e, in erg sec (esu)$^{-1}$ and the corresponding values of $c_2$ in cm deg*

| Method | Determinations | $h/e\times10^{17}$ | $c_2$ | Weight |
|---|---|---|---|---|
| Ionization potentials | 1 | 1.3753 | 1.4344 | 1 |
| Photoelectric effect | 3 | 1.3745 | 1.4336 | 3 |
| X-rays | 5 | 1.3758 | 1.4350 | 5 |
| Rydberg number | ? | 1.3787 | 1.4380 | 5 |
| Electron diffraction | 2 | 1.3767 | 1.4359 | 2 |
| Fine structure | | (1.3783) | (1.4376) | 0 |
| Weighted mean | | | 1.4358 cm deg | |
| Mean deviation | | | 0.0014 | |

It might be pointed out that according to Bond [86], all experimental determinations of $e/m$ are in reality determinations of (136/137) $(e/m)$. On Bond's theory the value of $c_2$ from the Rydberg number is reduced by about ¼ percent, or, in this case, from 1.4380 to 1.4344.

Perhaps it should also be mentioned that Anderson [87] on the basis of a pseudo-frictional effect between light quanta has deduced the relation

$$\sigma=\left(\frac{\pi^2}{90}\right)^{1/3}\frac{2^4\pi^{11}c^2h}{3^75^2c_2^4}=1.01\sigma \text{ (from eq. 10)}$$

This theory was apparently devised to explain discrepancies between experimental values of $\lambda_m T$ and $\sigma$ which have disappeared with the abandonment of the old value of $e$.

## VIII. SUMMARY

All of the experimental data available have been used to derive values of $c_2$. This was merely a matter of choice, and the same data can be used in each case to calculate values of the other radiation constants. For example, the relation between $\lambda_m T$ and $c_2$ is exact. Similarly, the values of $\sigma$ and $c_1$ listed on page 392 have been calculated from $c_2$. The values of $c_2$ from various sources are summarized in table 8, and the final mean value of $c_2$ there recorded will yield values of the other radiation constants which embody all the experimental data which have been considered.

TABLE 8.—*Summary of values of $c_2$ from all sources*

| Source | $c_2$ in cm deg | Weight |
|---|---|---|
| $\lambda_m T$ | 1.4361 ±0.0050 | |
| $\sigma$ | 1.4368 ± .0040 | |
| Optical pyrometry | 1.4364 ± .0020 | |
| Atomic constants | 1.4358 ± .0015 | |
| Weighted mean | 1.4362 ±0.001 | |
| Mean deviation | 0.0003 | |

It would seem that the probability is small that the true value of $c_2$ lies outside the limits 1.436 ±0.001 cm deg. The values of a set of mutually consistent constants derived from all available data are listed below.

$c_1 = (3.732 \pm 0.006) \times 10^{-5}$ erg cm$^2$ sec$^{-1}$
$c_2 = 1.436 \pm 0.001$ cm deg
$\lambda_m T = (2892 \pm 2) \times 10^{-4}$ cm deg
$\nu_m / T = (5890 \pm 4) \times 10^7$ deg$^{-1}$ sec$^{-1}$
$\sigma = (5.70 \pm 0.02) \times 10^{-5}$ erg sec$^{-1}$ cm$^{-2}$ deg$^{-4}$
$c = (2.9978 \pm 0.0002) \times 10^{10}$ cm sec$^{-1}$
$F = (2.8926 \pm 0.0003) \times 10^{14}$ (esu) mole$^{-1}$
$T_0 = 273.16 \pm 0.02$ deg
$R = (8.3142 \pm 0.0010) \times 10^7$ erg deg$^{-1}$ mole$^{-1}$
$k = (1.378 \pm 0.002) \times 10^{-16}$ erg deg$^{-1}$
$\epsilon = (4.800 \pm 0.004) \times 10^{-10}$ (esu)
$p = 1.00048$
$q = 0.99986$
$pq = 1.00034$
$h = (6.61 \pm 0.01) \times 10^{-27}$ erg sec
$h/e = (1.377 \pm 0.001) \times 10^{-17}$ erg sec (esu)$^{-1}$
$e/m = (5.273 \pm 0.002) \times 10^{17}$ (esu) $g^{-1}$
$M$ = Least mechanical equivalent of light $= (151 \pm 1) \times 10^{-5}$ watt ("new" lumen)$^{-1}$.
Calcite-grating space $= (3.0356 \pm 0.001) \times 10^{-8}$ cm.
Fine-structure constant (reciprocal $= 137.0 \pm 0.2$).

The writer has attempted to handle the data in such a manner as to secure results which reflected his own personal opinions as little as possible. An attempt has been made to avoid criticism by refusing to assign weights to published results or to apply corrections not pointed out by those who reported the original results. The practice of weighting values by different observers in the inverse ratio of the uncertainties which the observers attach to their own results seems a very questionable one.

In conclusion, it may be of interest to say something about the least mechanical equivalent of light, $M$. This is not a constant in the ordinary sense because it is not fixed by the units of length, mass, time, and luminous intensity but involves, in addition, the physiological and psychological characteristics which are arbitrarily assigned to some hypothetical individual designated as standard, that is, the so-called "ICI standard observer." In the past a determination of $M$ has been merely a matter of determining the luminous intensity of a black body at some measured temperature and then calculating

$M$ on the basis of $c_2$, $\sigma$ or $c_1$, and the selected standard observer. In terms of the present "International" candle, 1 cm² of a black body at the freezing point of pure platinum emits 58.9 $\pi$, or 185.0 $\pm$0.2 international lumens [88]. The freezing temperature of platinum is 1773.5 on the international scale ($c_2$=1.432). On January 1, 1940, a new system of photometric units is scheduled to go into effect. The numerical value of $M$, in terms of the "new" units, will increase by approximately 2 percent, because on that date the luminous emission from 1 cm² of a black body at the freezing point of pure platinum becomes 60 $\pi$ "new" lumens by definition. $M$, thereupon, becomes fixed by $c_2$, $\sigma$, and the standard observer (luminosity factors). On the basis of $c_1$=3.732$\times$10$^{-5}$ and $c_2$=1.436, we have that the freezing point of platinum is 2043.8° K and that $c_2/2043.8$=7.0261$\times$10$^{-4}$, so that

$$M=A\int_0^\infty L_\lambda \lambda^{-5}\left(e^{\frac{7.0261}{\lambda\times 10^4}}-1\right)^{-1}d\lambda,$$

where the values of $L_\lambda$ are the internationally accepted [80] luminosity factors describing the ICI standard observer and $A=c_1/60\pi$= 1.980$\times$10$^{-7}$ erg sec$^{-1}$ cm$^2$ ("new" lumen)$^{-1}$. From this relation $M$ is found to be 1.508$\times$10$^4$ ergs per "new" lumen second, or 0.001508 watt per "new" lumen. On the basis of $c_2$=1.432, $M$=0.00157 watt per "new" lumen, which is identical with the former value of $M$= 0.00160 watt per "international" lumen.

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# PREPARATION AND PROPERTIES OF β-*d*-2-DESOXYGALACTOSE

By Horace S. Isbell and William W. Pigman

ABSTRACT

The preparation of crystalline β-*d*-2-desoxygalactose, $C_6H_{12}O_5$, is described and its properties reported. It melts at 121° C and gives the pine-splinter and digitoxin reactions for desoxy sugars. With Fehling's solution the reducing power is about that of dextrose, but with less alkaline reagents like Benedict's solution its reducing power is less and varies widely with the boiling time. In 4-percent aqueous solution buffered with 0.001 *N* potassium acid phthalate, β-*d*-2-desoxygalactose gives $[\alpha]_D^{20} = +41$ initially, decreases in 5 minutes to a minimum of +37, and increases thereafter to an equilibrium value of +60.5. The heat of activation for the rapid mutarotation reaction is less than that of the slow mutarotation reaction. The proportions of the constituents responsible for the rapid reaction change with temperature more than the proportions of those which cause the slow reaction. The mutarotation of the new sugar shows that it establishes an equilibrium with an alpha pyranose modification and a labile substance.

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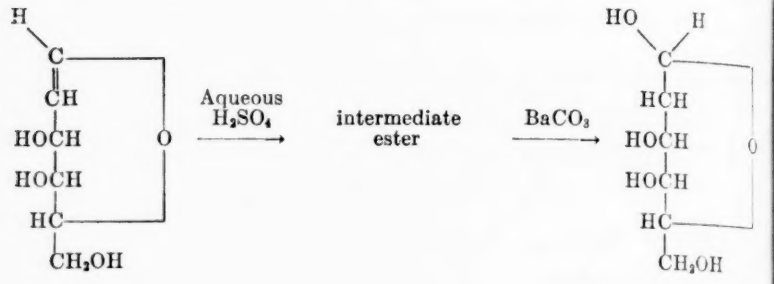
## I. INTRODUCTION AND DISCUSSION

Our previous investigations [1, 2, 3, 4][1] have shown that the configurations of the first five carbon atoms in the reducing sugars determine in large measure the position of the equilibrium which is established when the sugar is dissolved in water. The configuration of the carbon adjacent to the reducing group influences in marked degree the properties of the sugar and the relative proportions of the alpha and beta isomers. It is therefore of interest to investigate the 2-desoxy sugars in which the second carbon is not asymmetric.

In 1931 Levene and Tipson [5] reported the preparation of 2-desoxygalactose. This substance appeared to be suitable for our investigation because it is closely related to *d*-galactose, a sugar which had been carefully studied. We had on hand a quantity of galactal [6] from which we prepared desoxygalactose by the method of Bergmann and Schotte [7]. The sugar was obtained as described on page 398 by the following reactions:

[1] Figures in brackets indicate the literature references at the end of this paper.




Galactal — *β-d*-2-Desoxygalactose

Desoxygalactose, like galactose and other sugars which have opposite configurations for the groups on carbons 4 and 5, is particularly suitable for studying the interconversion of the pyranose and furanose modifications [8].

Different configurations for carbons 4 and 5 cause large differences in the optical rotations of the pyranose and furanose modifications. If carbons 4 and 5 are of different configuration, small changes in the proportions of the pyranose and furanose modifications can be detected by optical rotation measurements. The mutarotations of sugars which differ in the configurations of carbons 4 and 5 usually exhibit maximum or minimum values. When desoxygalactose is dissolved in water the optical rotation decreases to a minimum and then rises slowly until a constant value is reached. The changes reveal that a more levorotatory modification is formed from the parent sugar at a relatively rapid rate, while simultaneously, a more dextrorotatory substance is formed at a slower rate. More than three substances may be involved in the equilibrium state but the optical rotations do not suffice to prove the presence or absence of more than three substances. The heat of activation for the rapid reaction is less than that of the slow reaction. Presumably the rapid change in optical rotation is caused by a reaction analogous to the rapid mutarotation reaction of galactose which we have shown [8] to consist primarily in an alteration in ring structure. The slower mutarotation appears to be analogous to the mutarotation of glucose and other alpha and beta pyranose interconversions. If it be assumed that the sugar is a pyranose (an assumption which is probably correct), the crystalline sugar is the less dextrorotatory member of the alpha-beta pair, and since the oxygen ring lies to the right the sugar is classified as the beta modification. The proportions of the various modifications in the equilibrium solution change with temperature so that an alteration in temperature results in a "thermal mutarotation." The composition of the equilibrium solution and the rates of reaction are being investigated further in this laboratory and will be treated more fully in a subsequent publication.

## II. EXPERIMENTAL PROCEDURE

### 1. PREPARATION OF *β-d*-2-DESOXYGALACTOSE

Fifty grams of pure crystalline galactal was dissolved at 0° C in 700 ml of 5-percent sulfuric acid. The solution was allowed to stand overnight at 0° C. On the following day, 120 g of barium

carbonate was added. The mixture was heated with mechanical stirring to 60° C and kept at this temperature during working hours for about 1 week. Additional barium carbonate was added from time to time so that in all about 200 g was added. The excess barium carbonate was separated on a filter and the filtrate was boiled down to a thick sirup, which was taken up in about 50 ml of absolute ethyl alcohol. During the following night, crystallization occurred spontaneously. The crystals were separated and the mother liquor was evaporated in a desiccator over calcium chloride to give a second crop of crystals. The yield of crude desoxygalactose was 40 g.

The crude sugar was dissolved in water and after the addition of a small quantity of decolorizing carbon it was evaporated in vacuo to a thick sirup, which was diluted with three volumes of methyl alcohol and seeded with crystals from the first preparation. The resulting crystals were collected on a filter and washed with methyl alcohol and dried at room temperature over calcium chloride.

### 2. PROPERTIES OF β-*d*-2-DESOXYGALACTOSE

(a) *Melting point.*—120° to 121° C.

(b) *Analysis.*—Calculated for $C_6H_{12}O_5$: C, 43.90; H, 7.37. Found: C, 44.05; H, 7.35.

(c) *Iodine titration.*—During titration of the sugar by the method of Kline and Acree [9], 0.1683 g of the sugar consumed 21.74 ml of $N/10$ iodine solution; $C_6H_{12}O_5$ requires 20.50 ml.

(d) *Qualitative tests for desoxy sugars* [10].—A pine shaving impregnated with a solution of the sugar and exposed to warm vapors of aqueous hydrochloric acid gives the dark green coloration characteristic of desoxy sugars.

A very dilute solution of the sugar dissolved in acetic acid containing ferric sulphate carefully poured over sulfuric acid containing ferric sulfate gives a violet ring which fades into reddish-brown in the lower part of the tube. This reaction, which is sometimes called the digitoxin reaction, appears to be characteristic of 2-desoxy sugars [10].

(e) *Copper-reducing value.*—By the Munson and Walker method [11] 60-mg samples of the sugar gave 131.4, 131.2, and 131.2 mg of $Cu_2O$, and a 30-mg sample of the sugar gave 66.3 mg of $Cu_2O$. It requires 57.3 mg of dextrose to give 131.2 g of $Cu_2O$ and 28.4 mg of dextrose to give 66.3 mg of $Cu_2O$. Consequently, the reducing-power factor for the larger sample of desoxygalactose equals 57.2/60, or 0.95.

In copper solutions buffered with carbonates the sugar is oxidized *very slowly* and gives low reducing values unless the period of boiling is extended beyond the usual time. With Scales' method [12] for determining the cuprous oxide and using boiling periods of 6, 10, and 15 minutes, 20-mg samples of the sugar give cuprous oxide equivalent to 8.67, 13.57, and 17.32 ml of 0.04 $N$ iodine, respectively, for 6-, 10-, and 15-minute boiling periods. With a modified Scales method, using a 6-minute boiling period, it requires only 9.3 mg of glucose to give cuprous oxide equivalent to 8.67 ml of 0.4 $N$ iodine. Hence by this method the relative reducing value of desoxygalactose equals 9.3/20, or 0.46. The original Scales method calls for a boiling period of only three minutes, at which time desoxygalactose has only begun to reduce the copper reagent.

(f) *Optical-rotation measurements.*—The optical rotations as recorded in tables 1, 2, and 3 were measured in a 4-dm water-jacketed glass tube on a Bates saccharimeter. The equilibrium specific rotation was determined on separate samples at the concentration and temperature used in the mutarotation measurements. The velocity constants and equations representing the optical rotations were calculated by the method described by us on page 156 of reference [1]. The equations showing the specific rotations were obtained from the equations expressed in sugar degrees by multiplying the latter by the ratio of the equilibrium specific rotation to the equilibrium rotation as observed in sugar degrees.

The heats of activation were calculated by the Arrhenius equation,[2] using mutarotation constants obtained from the measurements in aqueous solutions buffered with potassium acid phthalate. The value (10,700) obtained for the more rapid reaction resembles the average (13,200) previously found for the rapid mutarotations of galactose, talose, arabinose, and ribose, while the value (15,650) obtained for the slow reaction resembles the average (16,900) [1, p. 165] previously found for the interconversion of the more common alpha and beta pyranose sugars. The activation constants correspond to a temperature coefficient [3] $k_{35}/k_{25}$ of 1.80 for the more rapid reaction and 2.35 for the slow reaction.

TABLE 1.—*Mutarotation of β-d-2-desoxygalactose at 20° C*

4 g in 100 ml of 0.001 *N* potassium acid phthalate solution (pH = 4.4).
$°S = -18.2\times10^{-.0234t} + 9.0\times10^{-.106t} + 28.26.$
$[\alpha]_D^{20} = -39.0\times10^{-.0234t} + 19.3\times10^{-.106t} + 60.5.$
$[\alpha]_D^{20} = +40.8$ initially; $+60.5$ at equilibrium.

| Time | Observed reading | $m_1\times10^3$ | Deviation | $m_2\times10^3$ |
|---|---|---|---|---|
| *Minutes* | °S | | | |
| 0 | ..... | ..... | ..... | ..... |
| 2.13 | +17.54 | ..... | 5.35 | ..... |
| 3.33 | +17.40 | ..... | 4.12 | 95 |
| 4.62 | +17.21 | ..... | 2.84 | 110 |
| 6.24 | +17.42 | ..... | 1.80 | 115 |
| 7.17 | +17.80 | ..... | 1.51 | 109 |
| 7.93 | +18.10 | ..... | 1.29 | 107 |
| 8.69 | +18.39 | ..... | 1.08 | 106 |
| 9.58 | +18.80 | ..... | 0.93 | 102 |
| 11.50 | +19.51 | ..... | .54 | 106 |
| 13.45 | +20.33 | ..... | .36 | 104 |
| 16.50 | +21.50 | ..... | .17 | 104 |
| 20.40 | +22.74 | ..... | ..... | ..... |
| 25.80 | +24.24 | 25.5 | ..... | ..... |
| 30.31 | +25.16 | 25.3 | ..... | ..... |
| 37.52 | +26.29 | 26.1 | ..... | ..... |
| 45.38 | +26.99 | 25.5 | ..... | ..... |
| 51.52 | +27.33 | 24.9 | ..... | ..... |
| 60.60 | +27.73 | 25.3 | ..... | ..... |
| 23 hr. | +28.26 | ..... | ..... | ..... |
| Average... | ..... | 25.4 | ..... | 106 |

[2] $2.3026 \log \frac{k_1}{k_2} = \frac{Q}{1.9864}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$
The heat of activation, $Q$, obtained from the mutarotation coefficient is an empirical constant.
[3] Log $k_{35}/k_{25} = Q/42{,}111$

TABLE 2.—*Mutarotation of β-d-2-desoxygalactose at 0.2° C*

4 g in 100 ml of 0.001 *N* potassium acid phthalate solution.

$°S = -16.72x10^{-.003594t} + 5.20x10^{-.0278t} + 31.06.$
$[\alpha]_D^{0.2} = -36.4x10^{-.003594t} + 11.3x10^{-.0278t} + 67.6.$
$[\alpha]_D^{0.2} = +42.5$ initially, $+67.6$ at equilibrium.

| Time | Observed reading | $m_1x10^3$ | Deviation | $m_2x10^3$ |
|---|---|---|---|---|
| *Minutes* | °S | | | |
| 0 | | | 5.20 | |
| 4.62 | +18.84 | | 3.87 | |
| 6.56 | +18.51 | | 3.29 | 36.3 |
| 8.73 | +18.49 | | 2.99 | 27.3 |
| 10.50 | +18.50 | | 2.77 | 24.7 |
| 13.73 | +18.43 | | 2.30 | 24.8 |
| 17.50 | +18.36 | | 1.77 | 26.4 |
| 21.85 | +18.50 | | 1.40 | 25.6 |
| 24.81 | +18.51 | | 1.07 | 27.7 |
| 29.83 | +18.81 | | 0.82 | 26.7 |
| 34.69 | +19.05 | | .54 | 28.4 |
| 39.48 | +19.38 | | .38 | 28.9 |
| 45.53 | +19.82 | | .24 | 29.5 |
| 59.67 | +20.85 | | | |
| 77.39 | +22.13 | 3.28 | | |
| 90.36 | +23.06 | 3.45 | | |
| 146.58 | +26.17 | 3.68 | | |
| 185.30 | +27.48 | 3.62 | | |
| 244.92 | +28.95 | 3.70 | | |
| 295.12 | +29.67 | 3.68 | | |
| 331.90 | +30.07 | 3.72 | | |
| 24 hr. | +31.06 | | | |
| Average | | 3.59 | | 27.8 |

TABLE 3.—*Mutarotation of β-d-2-desoxygalactose at 20° C*

4 g in 100 ml of water.[1]

$°S = -16.7x10^{-.0265t} + 7.0x10^{-.198t} + 27.1.$
$[\alpha]_D^{20} = -37.3x10^{-.0265t} + 15.6x10^{-.198t} + 60.5.$

| Time | Observed reading | $m_1x10^3$ | Deviation | $m_2x10^3$ |
|---|---|---|---|---|
| *Minutes* | °S | | | |
| 0 | | | | |
| 2.26 | +15.03 | | 2.51 | |
| 3.21 | +15.13 | | 1.79 | 155 |
| 4.10 | +15.12 | | 1.05 | 206 |
| 4.89 | +15.30 | | 0.62 | 231 |
| 6.59 | +16.25 | | .34 | 201 |
| 7.99 | +16.82 | | | |
| 11.25 | +18.66 | 26.3 | | |
| 13.49 | +19.79 | 27.0 | | |
| 15.12 | +20.52 | 27.2 | | |
| 20.92 | +22.48 | 26.9 | | |
| 25.44 | +23.59 | 26.8 | | |
| 29.68 | +24.35 | 26.5 | | |
| 40.12 | +25.60 | 26.1 | | |
| 50.09 | +26.22 | 25.5 | | |
| 60.36 | +26.63 | 25.8 | | |
| 20 hr. | +27.09 | | | |
| Average | | 26.5 | | 198 |

[1] Ordinary distilled water.

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# ACTION OF BAKER'S YEAST ON *d*-TALOSE

By Horace S. Isbell

ABSTRACT

It is shown that baker's yeast does not acquire the property of fermenting talose by growing on galactose- and talose-containing media.

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## I. INTRODUCTION

The four hexoses, *d*-glucose, *d*-mannose, *d*-fructose, and *d*-galactose are fermented by yeasts. Kinetic studies, made with different yeasts and different temperatures have shown that glucose, mannose, and fructose are fermented with approximately the same readiness. Many yeasts which ferment glucose are without action on galactose and the temperature coefficients and properties of the fermentation of galactose show that it is different from the fermentation of glucose. If the similar behavior of the epimeric sugars, glucose and mannose, is due to the rapid formation of a common intermediate substance during the fermentation, one might anticipate that *d*-talose, which is epimeric to *d*-galactose, would be fermented by the same yeasts which act on galactose. It is reported, however, that *d*-talose is not fermentable. This important observation was made with crude talose solutions before crystalline talose was available.[1] Since a quantity of pure crystalline *d*-talose had been prepared in this laboratory,[2] it seemed desirable to reinvestigate the subject.

Yeasts which do not ordinarily ferment galactose acquire the property of fermenting it by growth in a galactose-containing medium. In order to ascertain whether or not a talose-fermenting yeast could be obtained by growth in a talose-containing medium, a series of fermentations with baker's yeast was conducted under conditions similar to those which Kirby and Atkin [3] found suitable for the preparation of

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galactose-fermenting yeasts. The results were negative so far as the production of a talose-fermenting yeast is concerned. Even after growing three generations in the presence of talose, the yeast did not appear to have talose-fermenting properties.

## II. PREPARATION OF YEAST

Ten-milliliter portions of a solution containing 2.5 g of glucose, 2.5 g of galactose, and 1.5 g of yeast extract in 100 ml of water were placed in test tubes and sterilized by heating for 30 minutes in a steam autoclave at 110° C. This sterile solution is hereafter designed as the galactose medium. A sample of baker's yeast (Fleischmann's) was introduced into one of the test tubes containing the galactose medium and the mixture was incubated at 30° C. After 2 days the yeast was separated and introduced into a second tube containing 10 ml of the galactose medium and incubated again for 2 days, after which the yeast was transferred to a third tube containing 10 ml of the galactose medium and incubated a third time. The resulting yeast was decanted and washed with sterile water. This product was the "galactose yeast" used in the experiment reported in table 1.

A sterile solution containing 2.5 g of glucose, 2.5 g of *d*-talose, and 1.5 g of yeast extract in 100 ml of water was prepared and the process used for growing the galactose yeast was repeated with this solution as a medium. The growth of yeast was smaller than that obtained with the galactose medium, but appeared healthy. The product thus obtained was designated "talose yeast," even though it does not appear to have any talose-fermenting property.

## III. ACTION OF THE "GALACTOSE YEAST" AND THE "TALOSE YEAST" ON SOLUTIONS OF GLUCOSE, GALACTOSE, AND TALOSE

The galactose and talose yeasts obtained as described in the preceding paragraph were divided and introduced into solutions of glucose, galactose, and talose containing 2.5 g of glucose, galactose, or talose, and 2 ml of a nutrient solution per 100 ml. The nutrient solution contained 2.5 g of $NH_4NO_3$, 0.3 g of $KH_2PO_4$, and 0.25 g of $MgSO_4 \cdot 7H_2O$ per 100 ml. The solutions were incubated at 30° C and from time to time 10-ml portions were separated for optical-rotation measurements Before reading the samples the solutions were clarified by treating with 10 mg of normal lead acetate. After the samples stood for 2 hours at 20° C, they were read on a Bates' saccharimeter in a 2-dm tube.

Although both yeasts fermented glucose and galactose, neither yeast fermented *d*-talose. The galactose-fermenting property of the "talose yeast" was not necessarily acquired because the original baker's yeast had a small galactose-fermenting capacity. After the fermentation had been allowed to continue for 15 days, nearly all of the talose was reclaimed in the crystalline state from the residual liquors.

TABLE 1.—*Action of yeasts on solutions of d-talose, d-galactose, and d-glucose at 30° C*

| Time | *d*-Talose | *d*-Galactose | | *d*-Glucose | |
|---|---|---|---|---|---|
| | Optical rotation in 2-dm tube | Optical rotation in 2-dm tube | Percentage of sample fermented | Optical rotation in 2-dm tube | Percentage of sample fermented |
| GALACTOSE YEAST | | | | | |
| *Days* | °S | °S | | °S | |
| 0 | 2.90 | 11.80 | 0 | 7.00 | 0 |
| 1 | 2.94 | 10.46 | 11.4 | 5.30 | 24.3 |
| 2 | 2.88 | 9.09 | 23.0 | 3.55 | 49.3 |
| 4 | 2.98 | 6.52 | 44.8 | 0.50 | 92.9 |
| 6 | 3.02 | 3.30 | 72.0 | (a) | 100 |
| 8 | 2.96 | 0.11 | 99.1 | ..... | ..... |
| 15 | 2.95 | (a) | 100 | ..... | ..... |
| TALOSE YEAST | | | | | |
| 0 | 3.02 | 11.85 | 0 | 7.03 | 0 |
| 1 | 2.96 | 11.60 | 2.1 | 6.67 | 5.1 |
| 2 | 3.02 | 11.53 | 2.7 | 4.91 | 30.2 |
| 4 | 2.94 | 10.10 | 14.8 | 0.95 | 86.5 |
| 6 | 2.95 | 6.92 | 41.6 | (a) | 100 |
| 8 | 2.94 | 2.14 | 81.9 | ..... | ..... |
| 15 | 3.00 | (a) | 100 | ..... | ..... |

[a] Test for reducing sugar was negative.

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# HEAT AND FREE ENERGY OF FORMATION OF WATER AND OF CARBON MONOXIDE *

By Frederick D. Rossini

ABSTRACT

Thermodynamic data were combined to yield values for the heats and free energies, per mole, of the following reactions, with each substance in the thermodynamic standard state:

$H_2(g)+1/2O_2(g)=H_2O(liq)$, $\Delta H°_{298.16}=-285,795 \pm 40$ int. j ($-68,318.1 \pm 9.6$ cal), $\Delta F°_{298.16}=-237,163 \pm 47$ int. j ($-56,692.8 \pm 11.2$ cal);

$H_2O(liq)=H_2O(g)$, $\Delta H°_{298.16}=44,007 \pm 13$ int. j (10,519.7 $\pm 3.1$ cal), $\Delta F°_{298.16}=8597 \pm 4$ int. j (2055.1 $\pm 1.0$ cal);

$H_2(g)+1/2O_2(g)=H_2O(g)$, $\Delta H°_{298.16}=-241,788 \pm 42$ int. j ($-57,798.4 \pm 10.0$ cal), $\Delta F°_{298.16}=-228,566 \pm 47$ int. j ($-54,637.7 \pm 11.2$ cal);

$CO(g)+1/2O_2(g)=CO_2(g)$, $\Delta H°_{298.16}=-282,942 \pm 120$ int. j ($-67,636.1 \pm 28.7$ cal), $\Delta F°_{298.16}=-257,069 \pm 121$ int. j ($-61,451.2 \pm 29.0$ cal);

C (c, graphite) $+1/2O_2(g)=CO(g)$, $\Delta H°_{298.16}=-110,413 \pm 129$ int. j ($-26,393.8 \pm 30.8$ cal), $\Delta F°_{298.16}=-137,158 \pm 133$ int. j ($-32,787.0 \pm 31.8$ cal);

$H_2(g)+CO_2(g)=H_2O(g)+CO(g)$, $\Delta H°_{298.16}=41,154 \pm 127$ int. j (9837.7 $\pm 30.4$ cal), $\Delta F°_{298.16}=28,504 \pm 130$ int. j (6813.8 $\pm 31.1$ cal);

C (c, graphite) $+CO_2(g)=2CO(g)$, $\Delta H°_{298.16}=172,529 \pm 244$ int. j (41,242.3 $\pm 58.4$ cal), $\Delta F°_{298.16}=119,911 \pm 248$ int. j (28,664.2 $\pm 59.3$ cal).

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## I. INTRODUCTION

This report presents values for the heat and free energy of formation of water and carbon monoxide and for the heat and free energy of the water-gas and producer-gas reactions. Values for these thermodynamic quantities were calculated from calorimetric data on the heats of combustion of hydrogen, carbon, and carbon monoxide and appropriate other new data on the entropies of the various substances involved, on the heat of vaporization of water, and on corrections to the ideal thermodynamic state.

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For each reaction entirely in the gaseous phase, there was first calculated from calorimetric data the value of $\Delta H^\circ_{298.16}$, which is the value of the change in heat content associated with the given reaction at 25° C, with each reactant and product in the ideal state of unit fugacity (1 atmosphere).[1] Then from the entropies of the various gases, which have been evaluated statistically by various investigators from spectroscopic and other molecular data, there was calculated the value of $\Delta S^\circ_{298.16}$, which is the change in entropy associated with the given reaction at 25° C, with each reactant and product in the ideal state of unit fugacity. These values for the change in heat content and entropy were then combined by means of the relation

$$\Delta F = \Delta H - T\Delta S \tag{1}$$

to yield the value of $\Delta F^\circ_{298.16}$, which is the change in free energy associated with the given reaction at 25° C, with each substance in the selected standard state.

To each value reported there is attached an estimate of the uncertainty. Where possible, this uncertainty was evaluated by a method previously described [2];[2] in other cases conservative estimates of uncertainty were made.

The unit of energy used is the international joule, determined by standards of electromotive force and resistance maintained at this Bureau. Conversion to the conventional defined calorie was made by means of the factor 1/4.1833.

For conversion of the statistically calculated values of entropies and heat contents to the units of energy used in this paper, the value of the gas constant, $R$, was taken as $8.3145 \pm 0.0006$ absolute j degree$^{-1}$ mole$^{-1}$, or $8.3128 \pm 0.0008$ int. j degree$^{-1}$ mole$^{-1}$, or $1.98714 \pm 0.00019$ cal degree$^{-1}$ mole$^{-1}$. (The derivation of the values of these constants will be discussed in a later report.)

## II. SOURCES OF THE DATA; CALCULATIONS

### 1. VALUES OF $(dH/dP)_T$

In order to correct the values of $\Delta H$ obtained for 1 atmosphere to values of $\Delta H$ with each substance in the standard state, there are required values of $(dH/dP)_T$ for the gases at 25° C and 0 to 1 atmosphere.[3]

For the gases (except water) involved in the present calculations, the values of $H^{P=0} - H^{P=1}$ at 25° C range from $-0.5$ j/mole for $H_2$(g) to 41 j/mole for $CO_2$(g). While the correction to zero pressure is not significant for hydrogen, and barely so for oxygen and carbon monoxide, the correction was made for all the gases for the sake of consistency.

In table 1 are given values of $H^{P=0} - H^{P=1}$ at 25° C for the gases, hydrogen, oxygen, carbon monoxide, carbon dioxide, and mixtures of oxygen and carbon dioxide. For hydrogen and carbon dioxide, the values were calculated by means of the Beattie-Bridgeman equation of state with the constants given by these authors [3, 4]. For oxygen

[1] Following Lewis and Randall [1], the superscript zero attached to a symbol denotes the selected thermodynamic standard state, and the subscript denotes the absolute temperature to which it applies.

[2] Figures in brackets indicate the literature references at the end of this paper.

[3] The heat content of a gas in the ideal (hypothetical) standard state of unit fugacity of 1 atmosphere is the same as the heat content of the real gas at zero pressure. The standard state for a liquid or solid is taken as that of the real substance at a pressure of 1 atmosphere.

and mixtures of oxygen and carbon dioxide, the values were calculated from the published data of Rossini and Frandsen [5] on $(dE/dP)_T$ at 25° C and their unpublished data on the $P$–$V$–$T$ relations of mixtures of oxygen and carbon dioxide [6], together with the temperature coefficient given by the Beattie-Bridgeman equation of state for conversion to 25° C. For carbon monoxide, the value was obtained by extrapolation of values of $(dH/dP)_T$ calculated from values of $V$ and $T$ $(dV/dT)_P$ given by Deming and Shupe [7] for 100, 75, 50, and 25 atmospheres.

For $H_2O(g)$ at 25° C, the value of $H^{P=0}-H^{P=0.03122}$ was taken as 22.0 ±1.0 j/mole, from unpublished calculations by C. H. Meyers of this Bureau. This value is substantially identical with that obtained by extrapolating values of $(dH/dP)_T$ for $H_2O(g)$ reported by Collins and Keyes [8]. The value for the vapor pressure of water at 25° C was taken as 0.031222 ±0.00020 atmosphere [9].

TABLE 1.—*Values*[a] *of* $H^{P=0}-H^{P=1}$ *at 25° C*

| Substance | $H^{P=0}-H^{P=1}$ |
|---|---|
| | *j mole*$^{-1}$ |
| $H_2(g)$ | −0.48 |
| $O_2(g)$ | 8.06 |
| $CO(g)$ | 7.20 |
| $CO_2(g)$ | 41.4 |
| $[(1-x)O_2+xCO_2]$[b](g) | $8.06+15.9x+17.4x$[2] |

[a] The uncertainty in these values is of the order of several percent.
[b] The symbol $x$ denotes the mole fraction of $CO_2$.

## 2. HEAT, ENTROPY, AND FREE ENERGY OF VAPORIZATION OF WATER

The new calorimetric data of Osborne, Stimson, and Ginnings [10] yield [4] for

$$H_2O(liq)=H_2O(g) \tag{2}$$

$$\Delta H^{P=0.03122}_{298.16}=43{,}985 \pm 13 \text{ int. j mole}^{-1}. \tag{3}$$

Conversion to the ideal standard state yields

$$\Delta H^{\circ}_{298.16}=44{,}007 \pm 13 \text{ int. j mole}^{-1}. \tag{4}$$

For the entropy of the process,

$$\Delta S^{P=0.03122}_{298.16}=147.521 \pm 0.044 \text{ int. j deg}^{-1} \text{ mole}^{-1}. \tag{5}$$

For $H_2O(g)$ at 25° C and a pressure of 0.031222 atmosphere,

$$S_{ideal}-S_{real}=0.058 \pm 0.002 \text{ int. j deg}^{-1} \text{ mole}^{-1}, \tag{6}$$

from unpublished calculations by C. H. Meyers. For the ideal gas at 25° C, the entropy of compression to 1 atmosphere is

$$S^{P=1}-S^{P=0.031222}=-R \ln[1/0.031222]$$
$$=-28.817 \pm 0.020 \text{ int. j deg}^{-1} \text{ mole}^{-1}. \tag{7}$$

Combination of eq 5, 6, and 7 yields for the vaporization of water, according to eq 2,

$$\Delta S^{\circ}_{298.16}=118.762 \pm 0.048 \text{ int. j deg}^{-1} \text{ mole}^{-1}. \tag{8}$$

[4] 1 mole of water is taken as 18.0162 g [20].

For $H_2O(g)$ at 25° C and a pressure of 0.031222 atmosphere, the unpublished calculations of C. H. Meyers yield

$$F_{ideal}-F_{real}=4.7 \pm 1.2 \text{ j mole}^{-1}. \quad (9)$$

For the ideal gas at 25° C, the free energy of compression to 1 atmosphere is

$$F^{P=1}-F^{P=0.031222}=RT \ln[1/0.031222]=8592.2 \pm 3.0 \text{ int. j mole}^{-1}. \quad (9a)$$

For the vaporization of water at 25° C at its saturation pressure the change in free energy is zero:

$$\Delta F^{P=0.031222}_{298.16}=0.0 \text{ j mole}^{-1}. \quad (9b)$$

Combination of eq 9, 9a, and 9b yields for the vaporization of water, according to eq 2,

$$\Delta F^{\circ}_{298.16}=8597 \pm 4 \text{ int. j mole}^{-1}. \quad (10)$$

## 3. VALUES OF ENTROPIES

The values used for the entropies at 25° C are given in table 2, where the sources are also indicated.

TABLE 2.—*Values of entropies at 25° C, and of heat contents at 25° C referred to the absolute zero*

| Substance | $S^{\circ}_{298.16}$ | | $H^{\circ}_{298.16}-H^{\circ}_0$ | | Source of values |
|---|---|---|---|---|---|
| | *int. j deg$^{-1}$ mole$^{-1}$* | *cal[a] deg$^{-1}$ mole$^{-1}$* | *int. j mole$^{-1}$* | *cal[a] mole$^{-1}$* | |
| C(c, graphite) | 5.712 ±0.100 | 1.365 ±0.024 | 1053.8 ±12.5 | 251.9 ±3.0 | [11, 12] |
| $O_2$(g) | 205.090 ± .040 | 49.026 ± .010 | 8653.6 ± 3.0 | 2068.6 ±0.7 | [d] [11, 33] |
| $CO_2$(g) | 213.729 ± .040 | 51.091 ± .010 | 9370.6 ± 4.0 | 2240.0 ±1.0 | [d] [11, 14] |
| CO(g) | 197.958 ± .040 | 47.321 ± .010 | 8670.7 ± 3.0 | 2072.7 ±0.7 | [15, 16, 17] |
| $H_2$(g) | 130.644 ± .020 | 31.230 ± .005 | 8466.6 ± 2.0 | 2023.9 ± .5 | [18, 19] |
| $H_2O$(g) | 188.843 ± .064 | 45.142 ± .015 | 9905.6 ± 4.0 | 2367.9 ±1.0 | [b] |
| $H_2O$(liq) | 70.081 ± .080 | 16.752 ± .019 | ---------- | ---------- | [c] |

[a] The calorie is defined as 4,1833 int. j.

[b] Unpublished value calculated by H. L. Johnston using the actual rotational levels instead of those of a rigid rotator. The value obtained by adding to Gordon's [3] value of the entropy (calculated on the basis of a rigid rotator) the correction for rotational distortion evaluated by Wilson [24] is lower than the value calculated by Johnston by 0.038 j deg$^{-1}$ mole$^{-1}$.

[c] Calculated from eq 2 and 8 and the value for $H_2O$(g).

[d] The values for the entropies and heat contents previously given [11] for $CO_2$ and $O_2$ differ (but not significantly) from those given in this table, because of the change in the value taken for the gas constant $R$. However, no change occurs in the values of $\Delta S^{\circ}_{298.16}$, $\Delta F^{\circ}_{298.16}$, and $\Delta H^{\circ}_0$ previously given [11] for the formation of carbon dioxide from its elements.

## 4. VALUES OF $H^{\circ}_{298.16}-H^{\circ}_0$

For calculating values of $\Delta H^{\circ}_0$ from the values $\Delta H^{\circ}_{298.16}$, there are required values of $H^{\circ}_{298.16}-H^{\circ}_0$ for each of the substances involved in the reactions. These values and their sources are given in table 2.

## 5. HEAT AND FREE ENERGY OF FORMATION OF WATER

The data reported in 1931 [21] for the heat of combustion of hydrogen, together with a correction (−3.6 j/mole in $\Delta H$) to the ideal state of unit fugacity and a correction (−9.5 j/mole in $\Delta H$) for the change in the molecular weight (to 18.0162 g) of water [20], yield for

$$H_2(g)+1/2\ O_2(g)=H_2O \text{ (liq)} \quad (11)$$

$$\Delta H^{\circ}_{298.16}=-285{,}795 \pm 40 \text{ int. j mole}^{-1}. \quad (12)$$

Combination of eq 2, 4, and 12 yields for

$$H_2(g)+1/2O_2(g)=H_2O(g) \quad (13)$$

$$\Delta H^\circ_{298.16}=-241{,}788 \pm 42 \text{ int. j mole}^{-1}. \quad (14)$$

Combination of eq 1 and 14 with the entropies of $H_2(g)$, 1/2 $O_2$ (g), and $H_2O(g)$ yields for eq 13, the formation of gaseous water,

$$\Delta F^\circ_{298.16}=-228{,}566 \pm 47 \text{ int. j mole}^{-1}. \quad (15)$$

Combination of eq 2 and 10 with 13 and 15 yields, for eq 11, the formation of liquid water,

$$\Delta F^\circ_{298.16}=-237{,}163 \pm 47 \text{ int. j mole}^{-1}. \quad (16)$$

## 6. HEAT AND FREE ENERGY OF COMBUSTION AND FORMATION OF CARBON MONOXIDE

The data reported in 1931 [22] [5] for the heat of combustion of carbon monoxide, together with a correction (25.2 j/mole in $\Delta H$) to the ideal state of unit fugacity and a correction (−64.3 j/mole in ΔH) for the change in the molecular weight (to 44.010) of carbon dioxide (which determined the amount of reaction) [20], yield for

$$CO(g)+1/2O_2(g)=CO_2(g) \quad (17)$$

$$\Delta H^\circ_{298.16}=-282{,}942 \pm 120 \text{ int. j mole}^{-1}. \quad (18)$$

The correction of the observed value of $\Delta H$ at 1 atmosphere to that at zero pressure was made in the following way. Examination of the calorimetric data on the heat of combustion indicated that the reaction which actually occurred in the calorimeter, on the average, was

$$CO \text{ (g, 1 atm)}+0.89\ O_2\text{(g, 1 atm)}=(CO_2+0.39\ O_2)\text{(g, 1 atm)}. \quad (19)$$

To the value of $\Delta H$ (−282,967 ±120 int. j/mole of $CO_2$) observed for this process were added the values of $\Delta H$ (−7.2, −7.2, and 39.6 j, respectively) associated with the following three processes:

$$CO \text{ (g, 0 atm)}=CO \text{ (g, 1 atm)}, \quad (20)$$

$$0.89\ O_2 \text{ (g, 0 atm)}=0.89\ O_2 \text{ (g, 1 atm)}, \quad (21)$$

$$(CO_2+0.39\ O_2) \text{ (g, 1 atm)}=(CO_2+0.39\ O_2) \text{ (g, 0 atm)}. \quad (22)$$

Combination of eq 18 and the entropies of CO (g), 1/2 $O_2$ (g), and $CO_2$ (g) with eq 1 yields for the combustion of carbon monoxide, eq 17,

$$\Delta F^\circ_{298.16}=-257{,}069 \pm 121 \text{ int. j mole}^{-1}. \quad (23)$$

In a previous report [11] there was given for

$$C \text{ (c, graphite)}+O_2 \text{ (g)}=CO_2 \text{ (g)} \quad (24)$$

$$\Delta H^\circ_{298.16}=-393{,}355 \pm 46 \text{ int. j mole}^{-1} \quad (25)$$

$$\Delta F^\circ_{298.16}=-394{,}228 \pm 58 \text{ int. j mole}^{-1}. \quad (26)$$

[5] The three other modern determinations of the heat of combustion of carbon monoxide, by Awbery and Griffiths [25], Fenning and Cotton [26], and Roth and Banse [27], yield values in accord with eq 17 and 18 within their estimated limits of uncertainty, namely, ±480, ±210, and ±840 j/mole, respectively. See reference [28].

Combination of eq 18, 23, 25, and 26 with 17 and 24 yields for the formation of carbon monoxide from its elements in their standard states

$$C\ (c,\ graphite)+1/2\ O_2\ (g)=CO\ (g) \tag{27}$$

$$\Delta H^\circ_{298.16}=-110{,}413\ \pm 129\ \text{int. j mole}^{-1} \tag{28}$$

$$\Delta F^\circ_{298.16}=-137{,}158\ \pm 133\ \text{int. j mole}^{-1}. \tag{29}$$

### 7. WATER-GAS AND PRODUCER-GAS REACTIONS

Values of the heat and free energy of the water-gas reaction may be obtained by combining eq 13, 14, 15, 17, 18, and 23:

$$H_2\ (g)+CO_2\ (g)=H_2O\ (g)+CO\ (g) \tag{30}$$

$$\Delta H^\circ_{298.16}=41{,}154\ \pm 127\ \text{int. j mole}^{-1} \tag{31}$$

$$\Delta F^\circ_{298.16}=28{,}504\ \pm 130\ \text{int. j mole}^{-1}. \tag{32}$$

Similarly, from eq 17, 18, 23, 24, 25, and 26, there is obtained for the producer-gas reaction

$$C\ (c,\ graphite)+CO_2\ (g)=2\ CO\ (g) \tag{33}$$

$$\Delta H^\circ_{298.16}=172{,}529\ \pm 244\ \text{int. j mole}^{-1} \tag{34}$$

$$\Delta F^\circ_{298.16}=119{,}911\ \pm 248\ \text{int. j mole}^{-1}. \tag{35}$$

## III. SUMMARY

A summary of all the values of $\Delta H^\circ_{298.16}$ and $\Delta F^\circ_{298.16}$ is given in table 3, together with values of $\Delta H^\circ_0$, calculated from the values of $\Delta H^\circ_{298.16}$ and the appropriate values of $H^\circ_{298.16}-H^\circ_0$ from table 2.

TABLE 3.—*Summary of thermodynamic values*

| Reaction | $\Delta H°_{298.16}$ | | $\Delta F°_{298.16}$ | | $\Delta H°_0$ | |
|---|---|---|---|---|---|---|
| | *int. j mole*$^{-1}$ | *cal*[a] *mole*$^{-1}$ | *int. j mole*$^{-1}$ | *cal*[a] *mole*$^{-1}$ | *int. j mole*$^{-1}$ | *cal*[a] *mole*$^{-1}$ |
| $H_2(g)+1/2\ O_2(g)=H_2O(liq)$ | −285, 795 ±40 | −68, 318. 1 ±9. 6 | −237, 163 ±47 | −56, 692. 8 ±11. 2 | | |
| $H_2O(liq)=H_2O(g)$ | 44, 007 ±13 | 10, 519. 7 ±3. 1 | 8, 597 ±4 | 2, 055. 1 ±1. 0 | | |
| $H_2(g)+1/2\ O_2(g)=H_2O(g)$ | −241, 788 ±42 | −57, 798. 4 ±10. 0 | −228, 566 ±47 | −54, 637. 7 ±11. 2 | −238, 900 ±42 | −57, 108. 0 ±10. 0 |
| $CO(g)+1/2\ O_2(g)=CO_2(g)$ | −282, 942 ±120 | −67, 636. 1 ±28. 7 | −257, 069 ±121 | −61, 451. 2 ±29. 0 | −279, 315 ±120 | −66, 769. 1 ±28. 7 |
| $C$ (*a*, graphite)$+1/2\ O_2(g)=CO(g)$ | −110, 413 ±129 | −26, 393. 8 ±30. 8 | −137, 158 ±133 | −32, 787. 0 ±31. 8 | −113, 703 ±130 | −27, 180. 2 ±31. 1 |
| $H_2(g)+CO_2(g)=H_2O(g)+CO(g)$ | 41, 154 ±127 | 9, 837. 7 ±30. 4 | 28, 504 ±130 | 6, 813. 8 ±31. 1 | 40, 415 ±127 | 9, 661. 0 ±30. 4 |
| $C$(c, graphite)$+CO_2(g)=2\ CO(g)$ | 172, 529 ±244 | 41, 242. 3 ±58. 4 | 119, 911 ±248 | 28, 664. 2 ±59. 3 | 165, 612 ±244 | 39, 588. 8 ±58. 4 |
| $C$(c, graphite)$+O_2(g)=CO_2(g)$ | −393, 355 ±46 | −94, 029. 8 ±11. 0 | −394, 228 ±58 | −94, 238. 5 ±13. 9 | −393, 018 ±48 | −93, 949. 3 ±11. 5 |

[a] The calorie is defined as 4.1833 int. j.

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# HEATS OF COMBUSTION OF TETRAMETHYLMETHANE AND 2-METHYLBUTANE

By John W. Knowlton and Frederick D. Rossini

ABSTRACT

Measurements of the heats of combustion of gaseous tetramethylmethane (neopentane) and gaseous 2-methylbutane (isopentane) in oxygen, at 25° C and a constant total pressure of 1 atmosphere, to form gaseous carbon dioxide and liquid water, yielded the following values in int. kj/mole: tetramethylmethane, 3516.53 ±0.94; 2-methylbutane, 3528.03 ±0.62. Converted to kilocalories by means of the factor 1/4.1833, these values become, respectively, 840.61 ±0.23 and 843.36 ±0.15 kcal/mole.

Combination of these values with those previously reported from this laboratory for normal pentane shows that, in the gaseous state at 25° C and 1 atmosphere, the energy content of normal pentane is greater than that of 2-methylbutane by 8.09 ±1.08 kj, or 1.93 ±0.26 kcal, per mole, and greater than that of tetramethylmethane by 19.59 ±1.29 kj, or 4.68 ±0.31 kcal, per mole.

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## I. INTRODUCTION

Only one determination of the heat of combustion of tetramethylmethane (neopentane), that of Thomsen [1][1] in 1886, and only one of the heat of combustion of 2-methylbutane (isopentane), that of Roth and Pahlke [2][2] in 1936, are described in the literature. An estimate

[1] Figures in brackets indicate the literature references at the end of this paper.

[2] See, however, the numerical value quoted in the Landolt-Börnstein-Roth-Scheel Tabellen [3] from unpublished work of Roth and Macheleidt, which value was later withdrawn [4].

of the heat of combustion of tetramethylmethane was made by one of the writers in 1935 [17]. Reliable values for these thermochemical constants are needed because of the present-day importance of the pentanes in the petroleum and synthetic chemical industries. This paper describes the calorimetric determination of the heats of combustion of tetramethylmethane and 2-methylbutane.

## II. UNIT OF ENERGY AND MOLECULAR WEIGHTS

The unit of energy employed in this work is the NBS international joule, based upon standards of electromotive force and resistance maintained at the National Bureau of Standards. The values in terms of the fundamental unit are also converted to a conventional, defined calorie by means of the selected factor 1/4.1833, which is being used by practically all thermochemical laboratories in this country [5].

The molecular weights of water and of carbon dioxide are taken as 18.0162 and 44.010 g/mole, respectively [6].

## III. METHOD AND APPARATUS

The calorimetric method employed in the present investigation has been described previously [7, 8, 9] and the reaction vessel was the same as that used in the experiments on ethylene and propylene [9].

## IV. CHEMICAL PROCEDURE

### 1. PREPARATION AND PURITY OF THE MATERIALS

#### (a) TETRAMETHYLMETHANE

The tetramethylmethane was prepared and purified in the chemical laboratories of the Pennsylvania State College under the direction of Frank C. Whitmore. The compound was synthesized and partially purified by Ewald Rohrmann, following the method described by Whitmore and Fleming [10]. Fraction 5, consisting of about 135 g, or one-third of the synthetic material, had a freezing point about 1.5° C below that of pure tetramethylmethane. The time-temperature melting curve of this material indicated about 0.9 mole percent of impurity. The final purification of this fraction was accomplished by George H. Messerly and John G. Aston, who subjected it to fractional distillation in an all-glass, vacuum-jacketed, rectifying column packed with single-turn glass helices. The distillation was conducted at a pressure of 400 mm of mercury, with a reflux ratio of 5 to 1. Middle portions of about 39 g and 46 g were collected from two separate distillations and combined to form the material sent to the National Bureau of Standards. From the results of vapor pressure measurements, and a knowledge of the estimated amount of impurity in the material before the final purification, Messerly and Aston, by comparison of similar data on different lots of tetramethylmethane previously prepared by Whitmore and his coworkers [10, 18], estimated [3] the amount of impurity in the final tetramethylmethane to be about 0.3 mole percent.

To ascertain the ratio of carbon to hydrogen in the purified material, the authors performed a series of five combustion experiments, in

[3] In a private communication to the authors.

which the masses of carbon dioxide and water (about 4 g and 2 g, respectively) were determined by a procedure previously described [11, 20, 8]. These experiments yielded, for 6/5 times the ratio of the number of moles of $CO_2$ to the number of moles of $H_2O$ formed in the combustion, the average value 0.99999, with an uncertainty [5] of $\pm 0.00014$, which ratio would be 1.00000 for pure tetramethylmethane.

From the results of these analyses, it may be concluded that the small amount of impurity in the tetramethylmethane contained carbon and hydrogen in a proportion not far from that in tetramethylmethane itself. Such an impurity would have, within the limits of accuracy of the present measurements, substantially no effect upon the heat of combustion as measured.[4]

#### (b) 2-METHYLBUTANE

The 2-methylbutane was prepared at the Bureau International des Étalons Physico-Chimiques at Brussels, and its preparation and properties have been reported by Timmermans and Martin [19]. The purity of this material was ascertained at the National Bureau of Standards by means of time-temperature cooling curves and by determination of the ratio of carbon to hydrogen.

The freezing point, determined with a platinum resistance thermometer, was found to be $-160.04 \pm 0.05°$ C., which agrees well with the value $-160.0°$ C reported by Timmermans [21], who also used a platinum resistance thermometer. From the time-temperature cooling curve, the amount of liquid-soluble, solid-insoluble impurity was estimated to be less than 0.1 mole percent.

The ratio of carbon to hydrogen was determined, by the procedure previously described [11, 20, 8, 9], from 16 combustion experiments in which the masses of water and carbon dioxide collected were of the order of 2 g and 4 g, respectively. The average value found for 6/5 of the ratio of the number of moles of $CO_2$ to the number of moles of $H_2O$ was 1.00005, with an uncertainty [5] of $\pm 0.00016$.

#### (c) OXYGEN

The oxygen (prepared commercially from liquid air) used for the combustion of the hydrocarbons was purified by passage through a tube containing copper oxide at about 600° C, and then successively through Ascarite (a mixture of sodium hydroxide and asbestos), anhydrous magnesium perchlorate, and phosphorus pentoxide.

### 2. PURITY OF THE COMBUSTION REACTION

The tetramethylmethane, previously dried by passage of the gas through anhydrous magnesium perchlorate, was burned in an atmosphere of purified oxygen in the calorimetric reaction vessel [8]. In the products of combustion of the tetramethylmethane, no carbon monoxide was found in tests which would have detected an amount corresponding to about 0.00002 mole fraction of the total carbon.[5]

Since 2-methylbutane is normally a liquid (boiling point 27.9° C at 1 atm) at the temperature at which the experiments were performed, it was necessary to carry the hydrocarbon into the calorimetric reaction vessel [8] with an inert gas—helium in this case. The procedure, in

[4] See, for example, p. 40–41 of reference [20].

[5] The tests for carbon monoxide were made by E. C. Creitz of the Gas Chemistry Section of this Bureau

general, was the same as that previously used for normal pentane [8] and methyl and ethyl alcohols [7]. The helium was first purified by mixing with it somewhat more than the amount of oxygen required to burn all the combustible impurities, passing the gas through a tube containing copper oxide at about 600° C, and then successively through Ascarite, anhydrous magnesium perchlorate, and phosphorus pentoxide. The helium was then passed into a saturator, where it emerged in fine bubbles from a sintered glass plate into liquid 2-methylbutane. The saturator was kept at a temperature of 18° C, and the calculated composition of gas issuing from it was about 73 mole percent of 2-methylbutane and 27 mole percent of helium. This gas was then burned in an atmosphere of oxygen in the reaction vessel. In the experiments with 2-methylbutane, the products of combustion contained carbon monoxide in an amount, on the average, corresponding to about $0.00003_2$ mole fraction of the total carbon. This necessitated a correction of $+0.003_2$ percent to the observed mass of carbon dioxide to obtain the true measure of the amount of reaction, and also a correction of $+0.001_3$ percent to the observed heat evolved in the calorimetric combustion experiments in order to obtain the heat which would have been evolved had no carbon monoxide been formed.

The purity of the ignition process was checked by running a series of ignitions and extinctions of the flame, in order to exaggerate greatly any abnormal effect, and then comparing the small masses of carbon dioxide and water formed. For both tetramethylmethane and 2-methylbutane, the masses of carbon dioxide and water balanced, stoichiometrically, within the limits of error of the measurements.

### 3. DETERMINATION OF THE AMOUNT OF REACTION

In the experiments on tetramethylmethane, the amount of reaction was determined [7, 8, 11, 20] from the mass of water formed in the combustion, 1 mole (18.0162 g) of water being taken as equivalent to 1/6 mole of tetramethylmethane. In the experiments on 2-methylbutane, the amount of reaction was determined from the mass of carbon dioxide (corrected, where necessary, as indicated above) formed in the combustion, one mole (44.010 g) of carbon dioxide being taken as equivalent to 1/5 mole of 2-methylbutane. The change to carbon dioxide in the latter experiments was made because new data on the atomic weight of carbon [6] indicated that the molecular weight of carbon dioxide is now known with an uncertainty of not more than about $\pm 0.003$ percent, and a significantly greater precision is possible because of the greater mass (over twice that of the water) of carbon dioxide produced in the combustion.[6]

## V. CALORIMETRIC PROCEDURE

### 1. ELECTRICAL-ENERGY EXPERIMENTS

The data of the electrical-energy experiments for tetramethylmethane are given in table 1, and those for 2-methylbutane are given in table 2. The various quantities have the same significance as in former reports (see p. 17 of reference [11] and p. 254 of reference [9]). The uncertainty,[7] with regard to precision, of the average value from

[6] See references [5] and [13] for further discussion of this point.

[7] All the estimates of uncertainty given in this paper are made according to the procedure given in reference [5].

each of these two groups of experiments is $\pm 0.01_2$ percent. Although substantially the same calorimetric system was used for both the hydrocarbons, the values of the electrical-energy equivalent of the calorimeter, given in tables 1 and 2, differ because, at the end of the experiments on tetramethylmethane, and before the experiments on 2-methylbutane, an accident necessitated repairs which changed the mass of glass in the reaction vessel.

TABLE 1.—*Calorimetric results of the electrical-energy experiments for tetramethylmethane*

| Experiment number | $\Delta R$ [1] | $k$ | $K$ | $U$ | Electrical energy [2] | Mass of calorimeter water | Electrical-energy equivalent of calorimeter system [3] | Deviation from mean |
|---|---|---|---|---|---|---|---|---|
| | *Ohms* | *Min*$^{-1}$ | *Ohms* | *Ohms* | *Int. j* | *g* | *Int. j/abs. ohm* | *j/ohm* |
| 1 | 0.385713 | 0.001940 | 0.007479 | 0.000855 | 56,589.9 | 3530.29 | 149,943.1 | 7.5 |
| 2 | .396848 | .001947 | .007109 | .000501 | 58,341.2 | 3528.32 | 149,970.7 | 35.1 |
| 3 | .396303 | .001947 | .007097 | .000768 | 58,241.3 | 3529.93 | 149,938.9 | 3.3 |
| 4 | .397967 | .001955 | .007443 | .000813 | 58,368.5 | 3524.87 | 149,986.4 | 50.8 |
| 5 | .389261 | .001934 | .007345 | .000687 | 57,092.2 | 3525.36 | 149,950.6 | 15.0 |
| 6 | .390371 | .001938 | .007233 | .000798 | 57,374.5 | 3533.83 | 149,902.9 | −32.7 |
| 7 | .391788 | .001949 | .007326 | .000831 | 57,575.5 | 3533.67 | 149,928.4 | −7.3 |
| 8 | .390643 | .001927 | .007261 | .000381 | 57,494.7 | 3534.21 | 149,941.9 | 6.3 |
| 9 | .390541 | .001924 | .007290 | .000645 | 57,382.8 | 3531.22 | 149,928.2 | −7.4 |
| 10 | .389857 | .001924 | .007221 | .000480 | 57,306.3 | 3530.77 | 149,923.5 | −12.1 |
| 11 | .388390 | .001927 | .007301 | .000411 | 57,188.7 | 3533.72 | 149,877.8 | −58.1 |
| Mean | | | | | | | 149,935.9 | ±22.4 |

[1] The average temperature of the calorimeter was 24.94° C. for experiment 1; 24.95° C for experiments 5, 10, and 11; 24.96° C for experiments 6, 8, and 9; 24.97° C for experiment 7; 24.99° C for experiment 3; and 25.00° C for experiments 2 and 4.
[2] The time of electrical-energy input was 1,020.00 seconds in each experiment.
[3] For 3,530.00 g of water and an average temperature of 25.00° C. (See p. 416 regarding units.)

TABLE 2.—*Calorimetric results of the electrical-energy experiments for 2-methylbutane*

| Experiment number | $\Delta R$ [1] | $k$ | $K$ | $U$ | Electrical energy [2] | Mass of calorimeter water | Electrical-energy equivalent of calorimeter system [3] | Deviation from mean |
|---|---|---|---|---|---|---|---|---|
| | *Ohms* | *Min*$^{-1}$ | *Ohms* | *Ohms* | *Int. j* | *g* | *Int. j/abs. ohm* | *j/ohm* |
| 1 | 0.388380 | 0.001940 | 0.007485 | 0.000792 | 56,998.5 | 3533.01 | 149,830.8 | −22.9 |
| 2 | .410515 | .001941 | .007768 | .000543 | 60,346.1 | 3533.04 | 149,875.4 | 21.7 |
| 3 | .386512 | .001931 | .007560 | .000528 | 56,783.4 | 3534.91 | 149,848.9 | −4.8 |
| 4 | .385815 | .001958 | .007483 | .000525 | 56,632.4 | 3530.65 | 149,870.8 | 17.1 |
| 5 | .384867 | .001927 | .007515 | .000546 | 56,506.0 | 3532.79 | 149,844.7 | −9.0 |
| 6 | .385725 | .001934 | .007467 | .000594 | 56,606.4 | 3532.06 | 149,800.4 | −53.3 |
| 7 | .384723 | .001932 | .007575 | .000693 | 56,457.4 | 3532.78 | 149,855.8 | 2.1 |
| 8 | .384655 | .001934 | .007572 | .000732 | 56,459.0 | 3533.21 | 149,883.8 | 30.1 |
| 9 | .384395 | .001919 | .007582 | .000558 | 56,408.8 | 3531.18 | 149,872.9 | 19.3 |
| Mean | | | | | | | 149,853.7 | ±19.8 |

[1] The average temperature of the calorimeter was 24.92° C for experiment 9; 24.93° C for experiments 5, 6, and 7; 24.94° C for experiments 3, 4, and 8; 24.95° C for experiment 1; and 25.06° C for experiment 2.
[2] The time of electrical-energy input was 1,020.00 seconds in each experiment.
[3] For 3,530.00 g of water and an average temperature of 25.00° C. (See p. 416 regarding units.)

## 2. CORRECTION EXPERIMENTS

The process of ignition and extinction of the flame was checked, as in the previous investigations, by performing a series of ignitions and extinctions of the flame, and making a thermal balance of the sources and sinks of energy, namely, the "reaction," "vaporization," "gas," and "ignition" energies, each of which was evaluated as before [11, 8, 9].

## 3. REACTION EXPERIMENTS

The data of the reaction experiments for tetramethylmethane are given in table 3. The average value of the heat of combustion from this series of experiments has an uncertainty (with regard to precision) of ±0.024 percent.

The data of the reaction experiments for 2-methylbutane are given in table 4. The average value of the heat of combustion from this series of experiments has an uncertainty (with regard to precision) of ±0.013 percent.

TABLE 3.—*Calorimetric results of the reaction experiments for tetramethylmethane*

| Experiment number | $\Delta R$ [1] | $k$ | $K$ | $U$ | Electrical-energy equivalent of calorimeter system [2] | "Gas" energy | "Ignition" energy | "Vaporization" energy | Mass of water formed in the reaction | Heat of combustion at 25° C. | Deviation from mean |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Ohms* | *Min*$^{-1}$ | *Ohms* | *Ohms* | *Int. j/abs. ohm* | *j* | *j* | *j* | *g* | *Int. kj/mole* | *kj/mole* |
| 1 | 0.387473 | 0.001927 | 0.008018 | 0.000408 | 150,207 | −3.3 | 34.5 | 234.4 | 1.75582 | 3517.76 | 1.23 |
| 2 | .400669 | .001954 | .008529 | .000300 | 150,154 | −5.3 | 18.4 | 259.5 | 1.81706 | 3514.86 | −1.67 |
| 3 | .401127 | .001933 | .007440 | .000579 | 150,193 | −4.7 | 18.4 | 246.1 | 1.82224 | 3516.23 | −0.30 |
| 4 | .402122 | .001943 | .007688 | .000399 | 150,101 | −11.1 | 29.9 | 230.2 | 1.82532 | 3515.13 | −1.40 |
| 5 | .400458 | .001940 | .008055 | .000354 | 149,886 | −1.7 | 27.6 | 242.9 | 1.81281 | 3516.94 | 0.41 |
| 6 | .401858 | .001926 | .007240 | .000435 | 149,890 | −3.0 | 23.0 | 206.8 | 1.82319 | 3514.19 | −2.34 |
| 7 | .401585 | .001932 | .006654 | .000474 | 150,197 | −1.5 | 23.0 | 194.4 | 1.82598 | 3517.59 | 1.06 |
| 8 | .401609 | .001933 | .006304 | .000474 | 150,259 | −15.5 | 23.0 | 186.6 | 1.82871 | 3517.49 | 0.96 |
| 9 | .402761 | .001912 | .007979 | .000483 | 149,953 | −11.4 | 36.8 | 243.7 | 1.82380 | 3517.38 | .85 |
| 10 | .402813 | .001930 | .006931 | .000594 | 150,009 | −10.2 | 18.4 | 208.0 | 1.82827 | 3517.76 | 1.23 |
| | Mean | | | | | | | | | 3516.53 | ±1.15 |

[1] The average temperature of the calorimeter was 24.94° C for experiment 1; 25.01° C for experiments 2, 3, 5, 6, 7, and 9; and 25.02° C for experiments 4, 8, and 10.

[2] Includes the heat capacity of one-half the mass of liquid water formed in the reaction.

TABLE 4.—*Calorimetric results of the reaction experiments for 2-methylbutane*

| Experiment number | $\Delta R$ [1] | $k$ | $K$ | $U$ | Electrical-energy equivalent of calorimeter system [2] | "Gas" energy | "Ignition" energy | "Vaporization" energy | Mass of carbon dioxide formed in the reaction [3] | Heat of combustion [4] at 25° C | Deviation from mean |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | *Ohms* | *min*$^{-1}$ | *Ohms* | *Ohms* | *Int. j/abs. ohm* | *j* | *j* | *j* | *g* | *Int. kj/mole* | *kj/mole* |
| 1 | 0.399703 | 0.001937 | 0.005638 | 0.000260 | 150,021 | 2.5 | 20.5 | 249.9 | 3.69820 | 3528.84 | 0.81 |
| 2 | .400214 | .001952 | .006236 | .000229 | 150,040 | −1.8 | 41.0 | 272.7 | 3.69991 | 3527.58 | −.45 |
| 3 | .402146 | .001969 | .005514 | .000343 | 150,123 | 0.8 | 41.0 | 245.7 | 3.72322 | 3528.19 | .16 |
| 4 | .399143 | .001940 | .007268 | .000326 | 149,984 | 1.0 | 61.5 | 322.2 | 3.67844 | 3528.66 | .63 |
| 5 | .399971 | .001944 | .004914 | .000350 | 149,996 | 0.0 | 20.5 | 235.4 | 3.70652 | 3527.67 | −.36 |
| 6 | .399666 | .001923 | .006469 | .000343 | 149,815 | −.9 | 41.0 | 304.7 | 3.68745 | 3528.16 | .13 |
| 7 | .399844 | .001934 | .006187 | .000266 | 149,884 | .0 | 41.0 | 263.7 | 3.69336 | 3526.31 | −1.72 |
| 8 | .400181 | .001937 | .005591 | .000299 | 149,820 | .9 | 20.5 | 255.6 | 3.69858 | 3528.56 | 0.53 |
| 9 | .398234 | .001938 | .006723 | .000609 | 149,856 | 1.0 | 41.0 | 304.6 | 3.67060 | 3527.54 | −.49 |
| 10 | .400449 | .001924 | .005558 | .000275 | 150,010 | −0.4 | 41.0 | 257.1 | 3.70584 | 3527.93 | −.10 |
| 11 | .400088 | .001927 | .005261 | .000387 | 149,988 | 2.3 | 20.5 | 253.2 | 3.70348 | 3528.91 | .88 |
| Mean | | | | | | | | | | 3528.03 | ±0.57 |

[1] The average temperature of the calorimeter was 25.00° C for experiments 6 and 9; 25.01° C for experiments 1, 2, 4, 5, 7, 8, 10, and 11; and 25.02° C for experiment 3.

[2] Includes the heat capacity of one-half the mass of liquid water formed in the reaction.

[3] Includes a correction of +0.00$_2$ percent because of the presence of a small amount of carbon monoxide in the exit gases (see p. 418).

[4] Includes a correction of +0.00$_1$ percent because of the presence of a small amount of carbon monoxide in the exit gases (see p. 418).

## VI. RESULTS OF THIS INVESTIGATION

The data of this investigation yield for the heats of combustion of tetramethylmethane and 2-methylbutane, according to the reaction

$$C_5H_{12}(g)+8O_2(g)=5CO_2(g)+6H_2O(liq) \quad (1)$$

at 25° C and a constant total pressure of 1 atmosphere, the values [5] shown in table 5. With these values are given the over-all uncertainties [5].

TABLE 5.—*Results of the present investigation*

[Reaction: $C_5H_{12}(g)+8O_2(g)=5CO_2(g)+6H_2O(liq)$]

| Gas | Molecular formula | Heat of combustion $-\Delta H$ at 25° C and 1 atmosphere | |
|---|---|---|---|
| | | *Int. kj/mole* [1] | *kcal/mole* [1] |
| Tetramethylmethane | $C_5H_{12}$ | 3516.53±0.94 | 840.61±0.23 |
| 2-Methylbutane | $C_5H_{12}$ | 3528.03±0.62 | 843.36±0.15 |

[1] See p. 416 of text.

[5] The value for the heat of combustion of tetramethylmethane given in tables 3 and 5 differs slightly (+0.00$_3$ percent) from that reported preliminarily [12] because of the change in the accepted value for the molecular weight of water from 18.0156 to 18.0162 [6].

## VII. DATA OF PREVIOUS INVESTIGATIONS

### 1. TETRAMETHYLMETHANE

The literature contains only one previously reported determination of the heat of combustion of tetramethylmethane, that of Thomsen [1] in 1886. The tetramethylmethane used by Thomsen was prepared by converting trimethylcarbinol into tertiary butyl iodide and treating the latter with zinc methyl. From combustion experiments in which the masses of water and carbon dioxide were determined, Thomsen calculated the molecular formula of two different preparations of the hydrocarbon to be $C_5H_{11.78}$ and $C_5H_{11.64}$, respectively, instead of the desired $C_5H_{12}$. If the impurity was isobutene, this would indicate that the two lots contained, respectively, only about 87.6 and 79.5 mole percent of tetramethylmethane. If the impurity

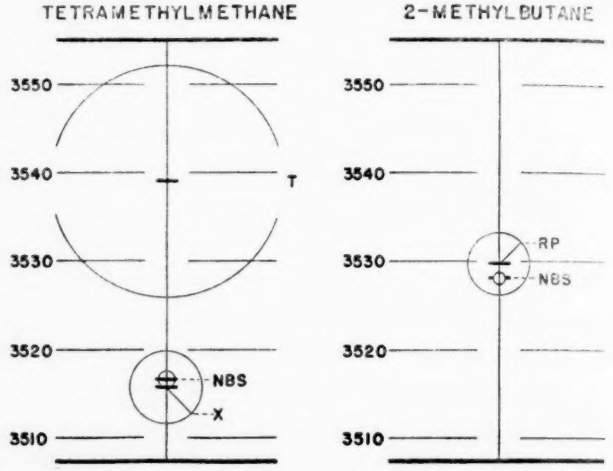


FIGURE 1.—*Plot of the various data on the heats of combustion of tetramethylmethane and 2-methylbutane.*

The scale of ordinates gives the heat of combustion, at 25° C and a constant total pressure of 1 atmosphere, in international kilojoules per mole. The average values, together with the estimated uncertainties (measured by the radii of the respective circles), are indicated as follows: T, Thomsen [1]; RP, Roth and Pahlke [2]; NBS, present investigation; X, value estimated for tetramethylmethane by one of the writers in 1935 [17].

was a pentene, the mole percentage of tetramethylmethane would be even less. Thomsen performed four combustion experiments in his constant-pressure flame calorimeter, using about 0.01 mole of hydrocarbon in each experiment. Making a reasonable correction for the amount of impurity, as Thomsen did, there is obtained from his data, for the heat of combustion of tetramethylmethane at 25° C and 1 atmosphere according to eq 1, the value $\Delta H = -3539 \pm 13$ int. kj, or $-846 \pm 3$ kcal, per mole.

In 1935 one of the writers [17] estimated, by extrapolation of the values determined in this laboratory for the heats of combustion of methane, ethane, propane, and isobutane, the value for the heat of combustion of tetramethylmethane, according to eq 1, to be $\Delta H = -3515.6 \pm 4.2$ int. kj, or $-840.4 \pm 1.0$ kcal, per mole.

The various values for tetramethylmethane are shown in figure 1.

### 2. 2-METHYLBUTANE

Only one investigation on the heat of combustion of 2-methylbutane is described in the literature, that of Roth and Pahlke [2][9] in 1936. These investigators also used 2-methylbutane from the Bureau International des Étalons Physico-Chimiques at Brussels, and burned the hydrocarbon in the gaseous phase in a bomb at constant volume, using about 0.006 mole of the hydrocarbon in each experiment. The data from the three experiments of Roth and Pahlke yield $\Delta H = -3529.7 \pm 3.6$ int. kj, or $-843.8 \pm 0.9$ kcal, per mole, for the heat of combustion of 2-methylbutane, according to eq 1, at 25° C and a constant total pressure of 1 atmosphere. This value is calculated on the basis of the unit of energy, the molecular weights, and the method of estimating uncertainties used in the present report.

The various values for 2-methylbutane are shown in figure 1.

## VIII. ENERGIES OF ISOMERIZATION OF THE THREE PENTANES

Combination of the values given in table 5 with the corresponding one previously reported for gaseous normal pentane [8, 13] yields directly the values of the energies of isomerization of the three pentanes in the gaseous state at 25° C and a total pressure of 1 atmosphere. For this purpose, the value previously reported for normal pentane is corrected, for the sake of consistency, by the factor $1.00003_3$ to conform with the newly accepted molecular weight of water [6], the mass of which from the products of combustion was used as a measure of the amount of reaction in the experiments on normal pentane. The value for normal pentane thus becomes $3636.12 \pm 0.83$ int. kj mole. The energies of isomerization so calculated for the three pentanes are given in table 6, and indicate that, with regard to the energy content of the molecule in the gaseous state at 25° C, the order of decreasing stability is tetramethylmethane, 2-methylbutane, normal pentane. While the values of the entropies of all three of the pentanes are not yet accurately known, it can be estimated from the available data [14, 15, 16, 18] that, when the entropies are taken into account, the free energies of the three isomers will be in the same order of decreasing stability, although the differences will be relatively less.

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The authors gratefully acknowledge their indebtedness to Frank C. Whitmore, John G. Aston, George H. Messerly, and E. Rohrman, of the Pennsylvania State College, for preparing and purifying the tetramethylmethane.

TABLE 6.—*Energies of isomerization of the three pentanes*

| Reaction | $\Delta H = \Delta E$ at 25° C and a total pressure of 1 atmosphere | |
|---|---|---|
| | *kj/mole* | *kcal/mole* |
| n-Pentane(g) = 2-methylbutane(g) | $-8.09 \pm 1.08$ | $-1.93 \pm 0.26$ |
| n-Pentane(g) = tetramethylmethane(g) | $-19.59 \pm 1.29$ | $-4.68 \pm 0.31$ |
| 2-Methylbutane(g) = tetramethylmethane(g) | $-11.50 \pm 1.13$ | $-2.75 \pm 0.27$ |

[9] See also footnote 2 on p. 415.

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WASHINGTON, January 26, 1939.

U. S. Department of Commerce National Bureau of Standards

RESEARCH PAPER RP1194

*Part of Journal of Research of the National Bureau of Standards, Volume 22, April 1939*

# A METHOD OF REDUCING THE EFFECT OF DISTURBANCES IN THE GALVANOMETER BRANCH OF A POTENTIOMETER CIRCUIT

By Frank Wenner

ABSTRACT

The method described automatically eliminates the effect of a thermoelectromotive force in the galvanometer branch and doubles the sensitivity of the galvanometer to a lack of balance of the potentiometer, thus reducing to half the effect of various types of electrical and mechanical disturbances.

In the measurement of small electromotive forces by means of a potentiometer, disturbances in the galvanometer branch frequently limit the accuracy attainable or increase the difficulties in obtaining a specified accuracy. These disturbances may be electrical or mechanical. In addition, the accuracy of the measurements may be limited by the sensitivity of the galvanometer or by the optical system of the galvanometer. Usually the most important disturbing factor in the galvanometer and other parts of the galvanometer branch is a thermoelectromotive force.

Under favorable conditions this thermoelectromotive force has a value in the range from $+1$ to $-1$ microvolt. When exceptional precautions are taken and an "all-copper circuit" galvanometer is used, this electromotive force usually has a value in the range from $+0.1$ to $-0.1$ microvolt. If, therefore, the accuracy of measurement is to be of the order of 0.01 microvolt, something in addition to the taking of exceptional precautions must be done to avoid the inclusion of the thermoelectromotive force in the galvanometer branch with the electromotive force being measured.

Various methods have been used in measuring or compensating the thermoelectromotive force in the galvanometer branch or galvanometer branch and potentiometer. The method most generally used [1] consists in balancing the potentiometer in the usual way and then making a second balance after reversing connections to the battery and to the source of the electromotive force being measured. The difference between the two readings of the potentiometer thus obtained is equal to twice the thermoelectromotive force in the galvanometer branch and potentiometer. The double measurement gives a correction which may be applied to each of a series of measurements, provided the thermoelectromotive force in the galvanometer branch and potentiometer remains constant throughout the series.

[1] H. Diesselhorst, Z. Instrumentenk. **28**, 7 (1908).

Another method consists in using a so-called "neutral resistor" and so-called "false zero" of the galvanometer.[2] This consists in replacing the source of the electromotive force being measured by a resistor which has the same resistance as the source and contains no source of electromotive force. Then with the battery circuit of the potentiometer open and the high sensitivity key in the galvanometer circuit closed, the scale of the galvanometer is so adjusted that the scale reading is zero. The same end is accomplished if, instead of adjusting the scale, the scale reading is noted and used as a zero. Each of these methods requires the use of a neutral switch, which will not introduce additional thermoelectromotive forces into the circuit.

Still another method consists in introducing into the galvanometer branch a potential drop equal in magnitude to the thermoelectromotive force but of opposite polarity.[3]

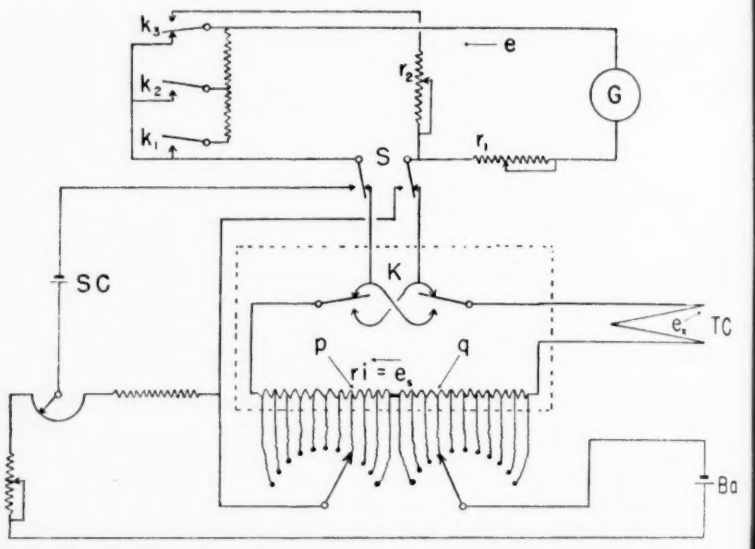


FIGURE 1.—*Potentiometer circuit showing double-pole double-throw key, K, in its relation to the galvanometer, thermocouple, and resistors of the potentiometer.*

In the first of these methods the thermoelectromotive force is measured. In the second and third it is compensated, but the compensation is accomplished in a different way. In the use of these methods, the thermoelectromotive force must be measured or compensated more or less frequently, depending on its rate of change and the accuracy desired in the measurements. A method which requires neither measurement nor compensation may be understood by a consideration of the circuit shown in figure 1. In this figure

*G*, the galvanometer

$r_1$, a resistor whose resistance together with other resistances in galvanometer circuit results in a suitable damping of the galvanometer;

$r_2$, a resistor for damping the galvanometer when the galvanometer keys are open;

[2] W. P. White, Phys. Rev. **25**, 344 (1907).
[3] H. B. Brooks and A. W. Spinks, BS J. Research **9**, 781 (1932) RP506.

$k_1$, $k_2$, and $k_3$, (low, intermediate, and high sensitivity) galvanometer keys

*M*, a double-pole, double-throw switch for changing the connection of the galvanometer from that used in measurements to that used in adjusting the current through the potentiometer;

*SC*, standard cell;

*K*, a double-pole, double-throw key necessary for the use of method described here;

*Ba*, the battery supplying the test current.

The portion of the circuit shown in the dotted rectangle is enclosed in a thermal shield and in general is so constructed as to be, with a normal ambient temperature, practically free of thermoelectromotive force. A construction resulting in an almost complete elimination or balance of thermoelectromotive forces has been described by Brooks and Spinks.[4] What has not been described previously is the double-pole double-throw key, *K*, and the method (or general procedure) used in establishing balances of the potentiometer. Inasmuch as a key suitable for use with the method is described in the following paper,[5] no detailed description will be given here. However, to fully realize the advantages of the method it should be understood that the key must be so constructed that a reversal of connections may be made in a time which is very short relative to the period of the galvanometer. During a reversal of connections, the resistance to an electromotive force in the galvanometer branch is either increased to infinity or decreased by an amount corresponding to the resistance of the "measuring circuit" of the potentiometer, plus the resistance of the source of the electromotive force being measured. Consequently, unless the reversal of connections is made quickly, the momentary decrease or increase of the current through the galvanometer will set the galvanometer coil in motion.

One of several possible ways of obtaining quick reversals of connections, without introducing objectionable features, is a construction such as is shown schematically in figure 2. It will be noted that connections are reversed without opening the circuit. Furthermore, the contacts, *s*, which also serve as stops, may be so adjusted that as the operating button is depressed or released the two halves of the switch change connections at substantially the same instant. It should be understood that the two halves of the key, instead of being placed end to end as shown, would be oriented in the same direction and placed side by side.

The general procedure in establishing a balance of the potentiometer is as follows:

1. The customary procedure is used up to the point at which with the full sensitivity of the galvanometer the deflection is not excessive. However, it is desirable that the galvanometer scale be so adjusted that the scale reading, with the keys $k_1$, $k_2$, and $k_3$ open (see fig. 1), differs considerably from zero or that the scale have its zero at one of its ends.

2. The key, $k_3$, is closed and from this point on is kept locked in the closed position.

[4] See footnote 3.

[5] R. P. Teele and S. Schuhmann, *A potentiometer for measuring voltages of 10 microvolts to an accuracy of 0.01 microvolt*, NBS J. Research **22**, 431 (1939) RP1195.

3. The potentiometer is so nearly balanced that the scale reading of the galvanometer becomes approximately the same as the initial scale reading.

4. With the key, $K$, alternately in one and then in the other of its two possible positions, for periods of time corresponding approximately to the period of the galvanometer, the potentiometer is so balanced that in the judgment of the observer the deflection of the galvanometer is not affected by changes in the position of the key, even though it may be affected by one, two, or more of several possible disturbing factors.

These four steps constitute a method of reducing the effect of disturbances in the galvanometer branch of a potentiometer circuit.

To see what is accomplished by the use of this method, consider first the case in which the only disturbing factor is a constant thermo-electromotive force in some part of the galvanometer branch.

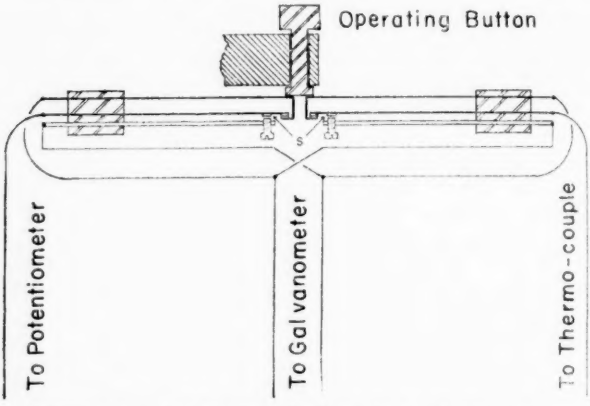


FIGURE 2.—*Quick-acting double-pole double-throw key.*

Let $d_0$=the scale reading corresponding to the mechanical zero of the galvanometer, that is, the scale reading which would have been obtained had the galvanometer circuit been opened at a point between the galvanometer and $r_2$ either just before or just after the establishment of a balance of the potentiometer,

$d_1$=the scale reading with the key, $K$, in the position shown in figure 1

$d_2$=the scale reading with the key, $K$, in the other position

$r$=the resistance of the potentiometer between potential and current branch points, that is, between $p$ and $q$ in figure 1

$i$=the current in the potentiometer

$e$=the electromotive force in the galvanometer branch

$e_s$=$ri$

$e_x$=the electromotive force being measured

$V$=the change in the scale reading resulting from unit change in the electromotive force in the galvanometer circuit.

With the key, $K$, in the position in figure 1

$$d_1-d_0=V(e+e_x-e_s). \tag{1}$$

With the key, $K$, in the other of its two possible positions

$$d_2-d_0=V(e-e_x+e_s). \tag{2}$$

From eq 1 and 2 it follows that

$$d_1 - d_2 = 2V(e_x - e_s). \tag{3}$$

Consequently, if

$$d_2 = d_1,\ e_x = e_s. \tag{4}$$

Equation 3 shows that the method obviates adjustments and readings of the galvanometer scale with either the galvanometer keys, $k_1$, $k_2$, and $k_3$, open or the galvanometer circuit open, automatically eliminates the effect of the thermoelectromotive force in the galvanometer branch, and in effect doubles the sensitivity of the galvanometer to a lack of balance of the potentiometer. The method also automatically eliminates the effect of the thermoelectromotive force in the resistor, $r_3$, and the key, $k_3$, when in either the open or closed position.

Continuing with the assumption that the only disturbance in the galvanometer branch is an electromotive force, if, in step 4 of the method, after the best possible adjustment of the potentiometer has been made, it is found that successive values of $d_1$ and $d_2$ are larger or smaller by approximately equal amounts, it is an indication that the electromotive force in the galvanometer branch is changing while the potentiometer is remaining balanced. Obviously, therefore, it is possible to establish accurate balances of the potentiometer even when the electromotive force in the galvanometer branch is changing, provided it changes slowly and at a fairly uniform rate. If, on the other hand, it is found that successive alternate differences between $d_1$ and $d_2$ are increasing or decreasing by approximately equal amounts, it is an indication that the electromotive force being measured is changing or that the current through the potentiometer is changing. Consequently, if the scale reading is changing gradually and in a fairly regular way, it is possible to determine whether the cause is changes in the electromotive force in the galvanometer branch or changes in the balance of the potentiometer.

The effects of other types of disturbances, such as mechanical vibrations, electromotive forces induced by neighboring circuits or by movement of the galvanometer leads in the earth's magnetic field and of other causes which in effect fix the magnitude of the least change in electromotive force producing a discernible change in the deflection of the galvanometer, are reduced to half. This results from the fact that, in effect, the method doubles the sensitivity of the galvanometer to a lack of balance of the potentiometer without affecting its sensitivity to disturbances.

A potentiometer made by the Leeds & Northrup Co. and a potentiometer made by the Rubicon Co. are equipped for the use of this method. Tests of these potentiometers have shown that in the measurement of very small electromotive forces, under normal laboratory conditions, an accuracy of 0.01 microvolt may be realized. In the paper which follows this [6] a potentiometer designed especially for the use of this method is described somewhat in detail, and results obtained in tests are given. The method described here is an adaptation to potentiometer measurements of the method which for many years has been used in those bridge measurements in which the accuracy of balances is such that the products of currents and resistances are matched to 0.1 and occasionally to 0.001 microvolt. However, it should be pointed out that, in bridge measurements, the resistance to

[6] R. P. Teele and S. Schuhmann, *A potentiometer for measuring voltages of 10 microvolts to an accuracy of 0.01 microvolt*, NBS J. Research, **22**, 431 (1939) RP1195.

an electromotive force in the galvanometer branch is not momentarily increased or decreased by the operation of the double-pole double-throw key or switch, since it is located in the battery branch. Nevertheless, the electromotive force induced in the bridge and galvanometer leads on reversing the current, would, in some cases, if not compensated, cause considerable movement of the galvanometer coil. One of the bridges is therefore equipped with a device for compensating this induced electromotive force. Furthermore, the double-pole, double-throw switch opens the circuit in the process of reversing connections, and it is not so constructed that it is free of thermoelectromotive forces. In addition, no sensitivity keys are used in the galvanometer branch. Consequently, the special equipment necessary to fully realize the advantages of the method and some of the initial steps in the establishment of balances are not the same in bridge measurements as in potentiometer measurements.

WASHINGTON, January 31, 1939.

U. S. DEPARTMENT OF COMMERCE NATIONAL BUREAU OF STANDARDS

RESEARCH PAPER RP1195

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# A POTENTIOMETER FOR MEASURING VOLTAGES OF 10 MICROVOLTS TO AN ACCURACY OF 0.01 MICROVOLT

By Ray P. Teele and Shuford Schuhmann

ABSTRACT

In connection with the development of a physical photometer it was found necessary to measure voltages of the magnitude of 10 microvolts to an accuracy of 1 part in a thousand. The design and construction of a potentiometer of the desired range and accuracy are described.

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## I. INTRODUCTION

The response of a thermopile used in a physical photometer being developed at the Bureau was found to be of the magnitude of 10 microvolts. It was desired to measure voltages of this magnitude to an accuracy of 1 part in a thousand. A potentiometer of the desired range and accuracy was designed and constructed.

When a small electromotive force of this magnitude is to be measured the most serious difficulty lies in the presence of extraneous thermal electromotive forces in the various parts of the measurement circuit. The major part of the apparatus to be described is designed to prevent or eliminate the effects of such electromotive forces.

## II. POTENTIOMETER CIRCUIT

A brief description of the potentiometer circuit and the method of using the potentiometer will suffice for a general understanding of the equipment. The special thermal shield, the reversing key, and the means employed to prevent or eliminate the effects of extraneous electromotive forces will then be discussed.

The electrical circuit [1] is shown in figure 1. In this figure, $e_x$ represents the unknown voltage to be measured; $A$, the thermal shield enclosing the "measurement circuit," consisting of the reversing key and the four-terminal resistor, $S$; $G$, the galvanometer; $R_B$, the balancing rheostat; $R$, a four-terminal resistance standard. With $e_x$ applied to the potentiometer, the resistance of $R_B$ is varied until the deflection of the galvanometer shows no change when the key, $K$, is operated. This condition indicates that the potential drop across the four-terminal resistor, $S$, which is due to the current in the balancing circuit, is equal and opposite to $e_x$. The current in the balancing circuit flows through $R$, and the potential drop across $R$ is measured by a suitable auxiliary potentiometer, in the present case a Wolff potentiometer of the Feussner type.

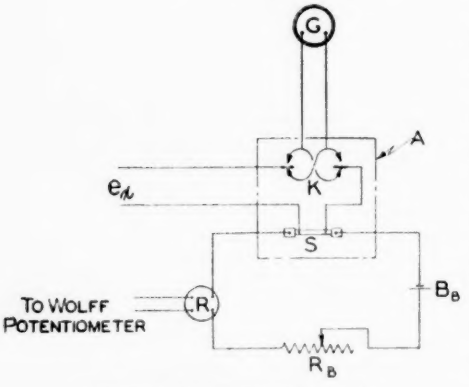


FIGURE 1.—*Electrical circuit.*

The reading of the Wolff potentiometer depends upon the values of $R$ and $S$. If $e_x$ is assumed to be 10 microvolts, or $10^{-5}$ volt, and $S$ is 0.01 ohm, the current, at balance, will be $10^{-3}$ ampere. This current flows through the 100-ohm resistance standard $R$. The potential drop across $R$ is, therefore, $10^{-1}$ volt, which is of a satisfactory magnitude for measurement. With the particular values of $S$ and $R$ chosen here, the balancing rheostat, $R_B$, needs to be adjustable from 0 to 10,000 ohms to cover a range of 2 to 2,000 microvolts (approximately) when a single lead storage cell is used to supply the balancing current. In addition to making the balancing battery and resistor of convenient size, these values for $S$ and $R$ mean that the first two dials of the auxiliary Wolff potentiometer indicate the whole microvolts, and the remaining three dials indicate the decimal parts of a microvolt.

When a lower accuracy is sufficient, a suitable milliammeter may be used to measure the current in the balancing circuit.

## III. THERMAL SHIELD

It is desirable to reduce parasitic electromotive forces to a value of 0.002 microvolt, that is, one-fifth of the desired accuracy. To accomplish this a number of expedients are employed, one of which is the isolation of the measurement circuit inside a thermal shield.

[1] J. C. Poggendorff, Ann Phys. Chem. **54**, 161 (1841); Lindeck and Rothe, Z. Instrumentenk **20**, 293 (1900); H. B. Brooks and A. W. Spinks, BS J. Research **9**, 781 (1932). RP506. This last paper contains a brief summary of the two references above and a discussion of basic potentiometer circuits.

The thermal shield is cast from an alloy of aluminum containing 15 percent of zinc. The zinc improves the machinability of the casting without reducing its thermal conductivity sufficiently to offset the gain in working qualities. The wall thickness is ⅜ inch.

The thermal shield is rectangular in shape and the division into halves is made along a diagonal plane. Figure 2 shows the thermal shield before final assembly. The division along a diagonal plane permits easy access to the parts when one-half of the shield is removed and also has the obvious advantage of requiring only one pattern for casting.

## IV. CAUSES OF EXTRANEOUS THERMAL ELECTROMOTIVE FORCES IN THE MEASUREMENT CIRCUIT

Thermal electromotive forces may arise from (1) temperature differences in the space within the thermal shield, (2) temperature differences between the springs and contacts of the reversing key, (3) temperature differences between the terminals of the four-terminal resistor, $S$, (4) heat conducted into the space within the thermal shield along the wires entering the thermal shield and along the actuating mechanism of the reversing key.

## V. REDUCTION OR ELIMINATION OF EXTRANEOUS THERMAL ELECTROMOTIVE FORCES

The various expedients used to reduce or eliminate the effects of the extraneous thermal electromotive forces are discussed according to the principal causes listed above. The various expedients used are each effective and the over-all result obtained is the product of the separate effectivenesses of the expedients used. The aim was to ensure that the precautions taken would be sufficient, and the necessity for each expedient was not determined. It is probable that an extensive study of the apparatus would show that simplification could be made by modifying or omitting some of the expedients used.

### 1. TEMPERATURE DIFFERENCES IN THE SPACE WITHIN THE THERMAL SHIELD

The perfect thermal shield would be a cavity in a block of metal of high thermal conductivity, with no openings of any kind, and thermally insulated from its surroundings. The necessity for providing for the entrance of wires and means for manipulating the reversing key, as well as the difficulties encountered in making such a thermal shield, make the ideal shield unattainable. The nearest approach to such a shield is an enclosure that is symmetrically divided. The symmetrical division of the enclosure gives two pieces of metal of very nearly equal thermal capacity. When these two halves are fastened together in such a manner that there is good thermal contact between halves, the enclosure has a symmetry of thermal capacity that greatly reduces the possibility of unequal distribution of temperature on the walls of the enclosure.

The thickness of the walls, the thermal capacity due to the mass, the thermal conductivity of the metal, and the thermal insulation are depended upon to maintain the walls of the thermal shield at the same

temperature throughout. When the walls of the thermal shield are at the same temperature throughout the space within the shield is free from temperature gradient in any direction and, consequently, apparatus located within the thermal shield is free from temperature differences which might cause thermal electromotive forces between component parts.

The thermal shield is enclosed in a box of balsa wood 2 inches thick to minimize the flow of heat to or from the surroundings. Such a heat flow might cause one part of the thermal shield to reach a temperature differing from that of some other part.

### 2. TEMPERATURE DIFFERENCES BETWEEN THE SPRINGS AND CONTACTS OF THE REVERSING KEY

The springs of the reversing key are of copper strip, which was cold-rolled to improve its elastic properties. The silver contact points are riveted in place. In order to minimize differences in temperature between any two silver-to-copper junctions which are in the measuring circuits, the fixed ends of all six springs were clamped between heavy copper blocks, with thin mica sheet for electrical insulation, and these blocks were in turn well connected mechanically and thermally to the side of the thermal shield. If, in spite of the precautions taken, the temperature of this portion of the shield should differ, however slightly from that of the rest of the shield, the symmetry of thermal capacity and thermal resistance of the six springs would still serve to maintain their free ends at the same temperature. The use of a small mica-insulated copper block to form a mechanical connection between the free ends of the inner or moving pair of springs provides for further equalization of temperature between these two springs.

In addition, the brass pieces, *B–B* in figure 3, make a partial enclosure within the main space, which gives still greater assurance that all parts of the reversing key are at the same temperature.

The reversing key is designed so that all junctions of dissimilar metals occur in adjacent pairs so arranged that a flow of heat in any direction will cause thermal electromotive forces of opposite sign and nearly equal magnitude in the circuit containing the key.

### 3. TEMPERATURE DIFFERENCES BETWEEN TERMINAL LEADS OF THE FOUR-TERMINAL RESISTOR

The resistor, *S*, is of the four-terminal type and is made in the form of a U. The open end is clamped, with mica, between copper blocks, and the copper blocks are bolted to the shield. The terminal leads are bent toward each other and brought as close together as possible without introducing any danger of a short-circuit between them, when air is the insulating medium. This brings the four terminal leads together into the same thermal environment. With the precautions taken in the design of the shield, this additional detail of grouping the terminal leads is felt to be adequate for eliminating any trouble from thermal electromotive forces at the terminals of the resistor.

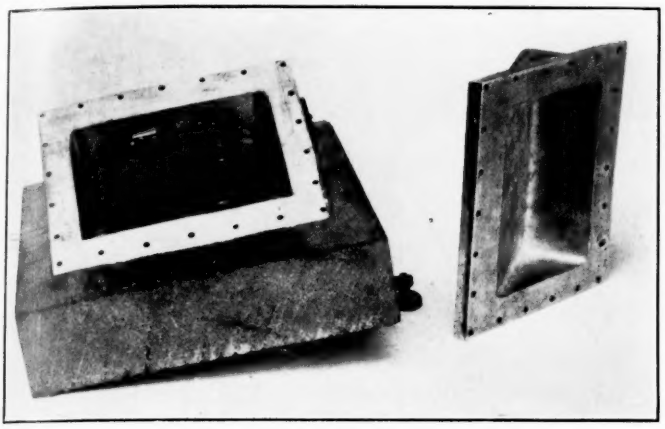

FIGURE 2.—*Thermal shield opened.*

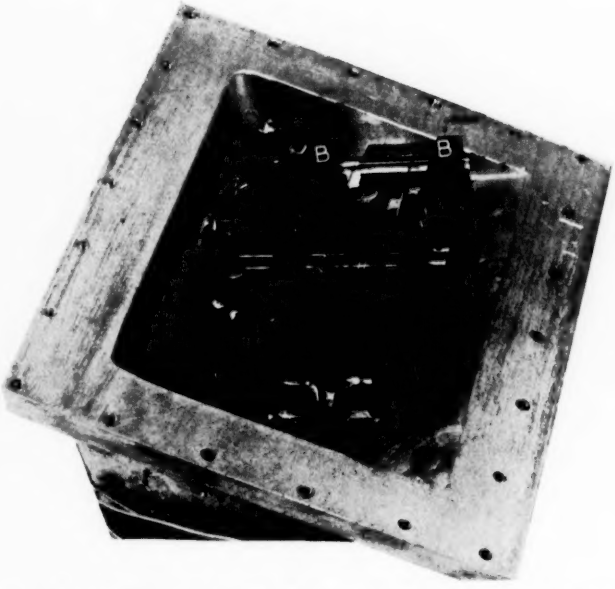


FIGURE 3.—*Interior of thermal shield with mechanical stops in place.*

### 4. TEMPERATURE DIFFERENCES CAUSED BY HEAT CONDUCTED INTO THE THERMAL SHIELD

#### (a) ALONG WIRES ENTERING THE SHIELD

The principle of the thermal "tie-down" [2] was used to divert any heat conducted along the wires onto the walls of the thermal shield. The wires enter the thermal shield through a copper block screwed to the outside of the shield. The wires are sealed with polyethylene phthalate resin, an electrical insulator but fairly good thermal conductor. About 95 percent of any heat conducted along the wires will flow to the walls of the thermal shield at this point. Just inside the shield each wire is coiled into a small helix. This helix offers a resistance to the flow of heat which increases the effectiveness of the transfer of heat at the copper block on the outside of the shield. The wires are then clamped, with mica, between copper blocks and the inner wall of the thermal shield. The heat transfer at this point is again about 95 percent complete. One more set of coils and another clamp are used before the wires are led to the various terminals. The transfer of heat from the wires to the walls of the thermal shield by these three thermal "tie-downs" is nearly complete, only 1 part in ten thousand is not diverted to the walls of the shield. In addition, the wires are led half way around the case in close proximity to the walls and to each other. Consequently, the end of each wire, where the soldered junction is made, must be at a temperature very close to that of the thermal shield and the space within the thermal shield.

#### (b) ALONG THE ACTUATING MECHANISM OF THE KEY

A key-actuating mechanism of usual construction would conduct heat at an undesirable rate from the hand of the operator into the thermal shield. To minimize the rate of transfer of heat, the reversing switch is operated by a linen thread, having a metal link where it passes through the case. The use of a thread is feasible, because, normally, the key remains closed in one direction, thus furnishing its own restoring force. When a lever made of hard rubber is depressed by the operator, the opposite end of the lever pulls the linen thread. Heat conducted from the operator's hand must travel along the hard-rubber lever and down the linen thread to the metal link, a path of comparatively high thermal resistance. The metal link causes most of the heat being transferred along the linen thread to flow to the walls of the thermal shield. The lower end of the metal link is attached to the movable springs by a linen thread. The hand of the operator is separated from the thermal shield by the balsa-wood enclosure.

## VI. OTHER SOURCES OF EXTRANEOUS ELECTROMOTIVE FORCES AND THEIR REDUCTION OR ELIMINATION

### 1. IN THE UNKNOWN-VOLTAGE CIRCUIT

There are several precautions that need to be observed in using the potentiometer. Obviously, the potentiometer will measure as a part of $e_x$ the resultant of any thermal electromotive forces in the circuit that connects this voltage to the potentiometer. To reduce these thermal electromotive forces as much as possible, any connections

[2] N. S. Osborne, H. F. Stimson, and E. F. Fiock, BS J. Research 5, 425 (1930) RP209.

should be protected from inequalities of temperature. A very satisfactory form of connector, shown in figure 4, was worked out for making these connections. Two copper bars with a copper screw in each end are clamped between metal blocks, with mica for electrical insulation. This reduces the temperature difference which can exist between the wires thus connected. The complete connector is thermally insulated and enclosed so as to exclude air currents from the junctions.

The connections must be allowed to come to thermal equilibrium with their surroundings before measurements can be made. It is apparent that connections can not be readily shifted. Consequently, when the polarity of the voltage to be measured is not known some means of reversing the potentiometer without disturbing the connections from the unknown voltage to the potentiometer is desirable.

Two reversing switches, one for reversing the current from the balancing battery, $B_B$ in figure 1, and the other for reversing the poten-

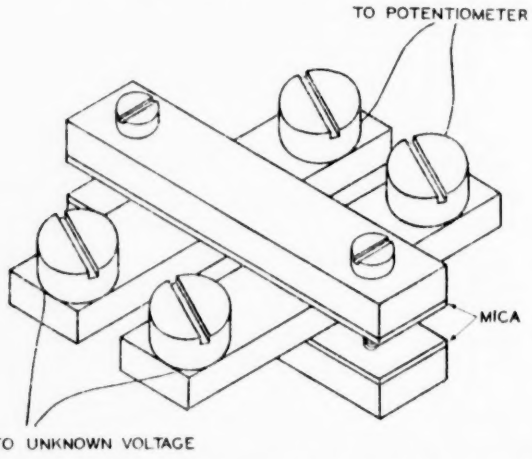


FIGURE 4.—*Connector for leads of unknown voltage circuit.*

tial leads from the standard resistor, $R$ in figure 1, will enable the potentiometer to be balanced for either polarity of the unknown voltage. Both of these reversing switches are in the balancing circuit, where their operation will not interfere with the immediate use of the potentiometer, since the extraneous electromotive forces thus generated are in series either with the relatively large electromotive force of the battery or with the relatively large potential drop across the 100-ohm resistor, $R$.

### 2. IN THE GALVANOMETER CIRCUIT

It is not practicable to maintain the galvanometer and galvanometer leads at a uniform temperature throughout. Consequently, there is almost always a resultant thermal electromotive force having its origin in that part of the galvanometer circuit beyond the reversing key. Under favorable conditions, for galvanometers of ordinary construction, this thermal electromotive force usually lies in the range from $+1$ to $-1$ microvolt. With an "all-copper-circuit" galvanometer

and taking exceptional precautions it usually lies in the range from +0.1 to −0.1 microvolt. Various procedures have been devised for measuring this electromotive force so that it may be added to or subtracted from the potential drop being measured. Also, various procedures have been devised for compensating for this electromotive force.[3] In addition to any thermal electromotive forces in the galvanometer or galvanometer leads, there may be other extraneous electromotive forces in this portion of the circuit, for example, those produced by leakage currents from other electrical circuits.

In the present potentiometer the manner in which the reversing key is used automatically eliminates the effects of extraneous electromotive forces having their origin in the galvanometer, and in effect doubles the sensitivity of the galvanometer to a lack of balance of the potentiometer, without changing its sensitivity to either electrical or mechanical disturbing factors. The function of the reversing key has been described in detail in the preceding paper.[4] For the convenience of the reader, a brief nontechnical discussion is given here. Figure 5 shows the portion of the circuit in which an extraneous electromotive force (if not taken into account) would introduce an error in the measurement.

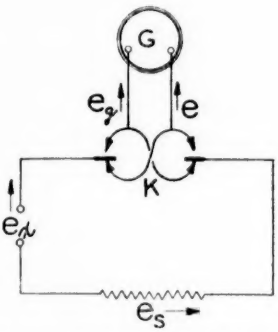


FIGURE 5.—*Portion of electric circuit.*

Let $e$ = the resultant of all extraneous electromotive forces in the galvanometer circuit. The quantity $e$ is considered as including any action upon that part of the galvanometer circuit beyond the reversing key which has any effect upon the scale readings, such as changes in the potential difference between the coil and case of the galvanometer, changes in the level of the galvanometer, and gradual shifts of the mechanical zero.

$e_g$ = the "unbalanced voltage," that is, the voltage due to any difference between $e_x$ and $e_s$.

$e_x$ and $e_s$ = the unknown voltage and the drop across the four-terminal resistor $S$, respectively.

Assuming exact equality of $e_x$ and $e_s$, we see that when the galvanometer reading does not change when the key, $K$, is operated it indicates (1) that $e_g$ and $e$ are both zero or (2) that $e_g$ is zero and $e$ is constant. As already pointed out on page 436, $e$ is probably not equal to zero and we usually have the second condition.

When $e_g$ is not zero and the key makes contact in one position, there is a deflection in one direction, and when the key is operated we have a similar deflection in the opposite direction. This is the equivalent of doubling the sensitivity of the galvanometer to any unbalanced voltage in the measurement circuit.

[3] H. B. Brooks and A. W. Spinks, BS J. Research **9**, 781 (1932) RP506.
[4] F. Wenner, *A method of reducing the effect of disturbances in the galvanometer branch of a potentiometer circuit*, J. Research NBS **23**, 425 (1939) RP1194.

## VII. ADJUSTMENT OF THE REVERSING KEY

The two pairs of stationary springs are held in position by stops which may be precisely adjusted in order to obtain the necessary accurate timing of the sequence of make and break contacts which constitute a reversal. Since the springs have a position of rest where all their free ends make contact, adjustment is made by varying the length of wires connected between capstans and small clips attached to the free ends of the stationary springs, that is, the free ends of the springs are pulled from their position of rest by the wires. These wires are insulated electrically but not thermally from their metal supports.

The optimum adjustment would be such that one pair of outer blades would make contact at the exact instant the other was disengaged by the moving pair. Since the system is mechanical, this adjustment is never perfectly made, so it becomes necessary to choose whether the transient condition shall be a short-circuit or an open-circuit.

This choice is made considering the magnitude of the measured electromotive force and the characteristics of the galvanometer, with the object of causing the least momentary change of the current through the galvanometer (assuming balance for the measuring circuit). In any case the adjustment is made as near as possible to optimum and in operation the key is depressed quickly, in order that the time interval between steady states of the current may be very short.

## VIII. TESTS AND PERFORMANCE

In order to test the effectiveness of the measures employed to eliminate the effects of extraneous electromotive forces in the vital parts of the circuit and to learn the operational characteristics, the reversing key and four-terminal resistor, enclosed in the thermal shield, were set up as for use, employing a high-sensitivity galvanometer.

A small all-copper shunt, well-insulated thermally, and with its potential terminals symmetrically placed and insulated from each other electrically but not thermally, was connected at leads $e_x$, figure 5. A known small current flowed through this shunt, which served to determine the galvanometer sensitivity without introducing any spurious thermal electromotive force.

The sensitivity of the galvanometer was found to be about 50 mm (double deflection) per microvolt. Upon removing the current connections from the shunt (leaving only thermal electromotive forces), it was found that on days when there was freedom from wind and magnetic disturbances, operating the key produced no discernible change in the galvanometer index reading. (The index could ordinarily be read to about 0.2 mm and changes of 0.1 mm were detectable.) This test indicated that thermal electromotive forces in the measuring circuit were certainly less than 0.002 microvolt.

The effect of a relatively large thermal electromotive force in the galvanometer circuit was also investigated. The all-copper shunt was used to supply 1 microvolt in the galvanometer circuit and the same procedure as above was followed except that the copper $e_x$ leads were short-circuited. Although the index reading was altered from

that obtained in the first test, again there was no noticeable change upon reversal.

Finally, a coil of silk-covered copper wire, thermally insulated, was connected at $e_x$ (fig. 5), leaving the potential difference of a microvolt in the galvanometer circuit. The resistance of this coil was equal to the external critical-damping resistance (about 60 ohms) of the galvanometer. In this case the operation of the reversing key produced a noticeable change in index reading, which appeared to be a result of a small residual thermal electromotive force in the damping resistor and not ascribable to an impulse caused by the operation of the key.

From the above tests it can be seen that with this apparatus it is possible to measure potential differences of the order of 1 microvolt to at least 0.2 percent, even though the galvanometer circuit itself contains an electromotive force of a microvolt. However, as pointed out above, it is advisable to keep the latter electromotive force small so as to minimize any impulse caused by the operation of the key. When this electromotive force is small its variation is also small.

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The authors are indebted to many members of the staff of the National Bureau of Standards for suggestions and advice. Dr. Wenner suggested the use of the reversing key and reviewed the design before construction started.

WASHINGTON, January 20, 1939.

U. S. Department of Commerce National Bureau of Standards

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# SOLUBILITY OF COLORED GLAZES IN ORGANIC ACIDS

By R. F. Geller and A. S. Creamer

ABSTRACT

The purpose of this study was to determine primarily which, if any, of the glazes tested constituted a health hazard because of lead or other toxic oxides which might be dissolved from them and, secondarily, to develop suitable test procedures for future control work.

A conference of representatives of the U. S. Potters Association, the Food and Drug Administration of the U. S. Department of Agriculture, and the National Bureau of Standards was held, and a series of accelerated and simulative service tests were outlined. These tests were made on specimens from six cooperating manufacturers.

It was shown that the amount of lead extracted by pouring hot distilled vinegar (5-percent acetic acid) or a 0.5-percent solution of citric acid into a cup and leaving it to cool in contact with the glaze for ½ hour would be as much or more than the lead normally extracted by jams and fruit juices. With the same or a similar test procedure, a citric-acid solution of 10-percent strength may be required to indicate how much lead might be taken up by lemonade or vinegar.

The results indicate also that glazes of only one color among those tested constitutes a probable health hazard. However, two other glazes from one manufacturer were found to be marginal, and a third may cause trouble if indicated corrective measures, such as a preliminary acid wash, should be neglected by the manufacturer.

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## I. INTRODUCTION

Accounts of the earliest investigations and regulations regarding the toxicity of lead in ceramic glazes have been summarized by Mellor [1] and by Koenig.[2]

More recently, investigations in Massachusetts [3] established that water containing as little as 0.1 part per million of lead produced symptoms of poisoning, and Jackson and Jackson [4] found that 1.7 parts per million of lead in cider gave acute symptoms of poisoning to the consumers. Considerable helpful information on the contamination of foods may be found in a report by G. W. Monier-Williams,[5] and W. P. Mason [6] stated that in the writer's opinion, no water to be

[1] J. W. Mellor, *The durability of pottery frits, glazes, glasses, and enamels in service*, Trans. Eng. Ceram. Soc. **34**, 113 (1934-35).
[2] J. H. Koenig, *Lead frits and fritted glazes*, Ohio State Eng. Exp. Sta. Bul. 95 (July 1937).
[3] Wade Wright, C. O. Sappington, and Eleanor Rantoul, J. Ind. Hygiene **10**, 234 (1928).
[4] M. C. N. Jackson and L. N. Jackson, The Lancet, **223**, 717 (1932).
[5] Report on Public Health and Medical Subjects No. 29 of the Ministry of Health, London (1925).
[6] Examination of Water (J. Wiley & Sons, Inc., New York, N. Y.).

used for drinking purposes should contain lead compounds in quantity greater than what would correspond to 0.5 part per million of metallic lead. Recently the U. S. Department of Agriculture established the tolerance of 0.025 grain of lead per pound of food (equivalent to about 3.57 parts of Pb per million parts of food), based upon investigations made by the U. S. Public Health Service. There is reason to believe, however, that a tolerance for "lead" in solid foods may be too lenient for application to lead ingested in solution as the salt of an organic acid. Therefore, the tolerance of 0.5 part per million in drinking water should not be lost sight of.

The present investigation was occasioned by a specific case of nausea believed to have been caused by tea flavored with lemon juice and drunk from a green cup, which came to the attention of the Food and Drug Administration. The matter was referred to the National Bureau of Standards, and a conference, attended by representatives of the U. S. Potters Association, the Food and Drug Administration, and the National Bureau of Standards, was held on May 21, 1938. A series of tests, to be made in cooperation with six manufacturers, was outlined, and the results of these tests are here reported.

## II. PURPOSE

The purpose of the work was threefold: (a) to develop test procedures for the treatment of the ware and for the analysis of the dissolved materials; (b) to correlate the results of relatively rapid and standardizable laboratory tests with those obtained under service conditions; and (c) to determine if any of the representative glazes submitted might constitute a health hazard.

## III. MATERIALS AND METHODS

Bowls, fruit dishes, and cups were submitted by the 6 cooperating companies, and usually 1 dozen specimens of each shape and color were available. Four colors (tangerine, yellow, bright green, and cobalt blue) were submitted by each manufacturer, but additional colors and shades were submitted by some. The maximum number from one concern was 20 colors.

A number of test methods were tried, but all except those given in table 1 were discarded. The discarded methods included heating on a steam bath or holding at "room temperature." Both involve temperature conditions difficult, if not impossible, to duplicate under ordinary conditions. The symbol accompanying each test was adopted for convenience in designating that test in the figures.

Unless otherwise designated in the table, the lead dissolved was determined by extraction with diphenylthiocarbazone, called "the dithizone method."[7] In the case of fruit juices and jams it was necessary to ignite and take up the residue in acid. Determination by precipitation as the sulfide with $H_2S$ followed customary chemical procedure. The amount of lead present was approximated by colorimetric comparison with standards containing 0.5, 1, 2, 4, and 6 parts of Pb per million parts of solution. If more than 6 parts per million were present in the test solution, an aliquot portion was used.

[7] The procedure used was essentially that in *Method for determining lead in food*, J. Assn. Official Agr. Chem. **17**, 123 (1934), separate copies no longer available, and in *Method for determining lead in canned food*, J. Assn. Official Agr. Chem. **18**, 315 (1935). Copies are obtainable from the Association (Box 540, Benjamin Franklin Station, Washington, D. C.).

TABLE 1.—*Test methods*

[Methods 1, 2, 10, 14, 15, and 16 are primarily for laboratory work; methods 3 to 9, inclusive, and 11 to 13, inclusive, were designed to simulate conditions in service, i. e., home or restaurant use]

| Test number | Symbol | Method |
|---|---|---|
| 1 | WV<br>½<br>$H_2S$ | A cup or fruit dish, into which 150 ml of boiling white vinegar (about 5-percent acetic acid) had been poured, was covered with a 3-liter beaker to protect it from drafts. After ½ hour the vinegar was removed to a Pyrex flask and subjected to the $H_2S$ test for lead.[a] |
| 2 | WV<br>½ | Same as test 1, except that lead is determined by the dithizone method.[b] |
| 3 | PJ<br>70°<br>2 da | A cup containing 150 ml of unsweetened pineapple juice was kept for 2 days in a room maintained at 70° F. |
| 4 | GFJ<br>70°<br>2 da | Same as test 3, except that unsweetened grapefruit juice was used. |
| 5 | ½ CAc<br>70°<br>2 da | Same as test 3, except that 0.5 percent of citric acid was used to simulate lemonade. |
| 6 | BV<br>70°<br>2 da | Same as test 3, except that brown vinegar (4.4-percent acidity) was used. |
| 7 | WV<br>70°<br>2 da | Same as test 3, except that distilled vinegar (5-percent acidity) was used. |
| 8 | WV<br>40°<br>2 da | Same as test 7, except that the specimens were held 2 days in a refrigerator at 40° F. |
| 9 | WV<br>RT<br>2 da | Same as test 7, except that the specimens were held at room temperature 85°±5° F. |
| 10 | WV<br>122°<br>1 da | Same as test 7, except that the specimens were held 1 day at 122° F (50° C) and the lead was determined by $H_2S$ precipitation. |
| 11 | CJm<br>RT<br>60 da | Specimens containing cherry jam were held at room temperature (80°±10° F) for 60 days. |
| 12 | SJm<br>RT<br>7 da | Specimens containing strawberry jam were held at room temperature (80°±10° F) for 7 days. |
| 13 | SJm<br>RT<br>60 da | Same as test 11, except that strawberry jam was used. |
| 14 | ½ CAc<br>½ hr | Same as test 1, except that a solution containing 0.5 percent of citric acid and 0.25 percent of gelatin was used. |
| 15 | CAc<br>½ hr | Same as test 14, except that the solution contained 1 percent of citric acid. |
| 16 | 10CAc<br>½ hr | Same as test 2, except that a solution containing 10 percent of citric acid was used. |

[a] This test may give too high values for lead because other metals, such as copper, which may be present also, are precipitated. The test was suggested to the industry for control and development work shortly after the conference held in May 1938 and became known as the National Bureau of Standards Tentative Test. It is described in the National Bureau of Standards Technical News Bulletin 255, July 1938.

[b] The dithizone extraction, followed by electrolysis, is a specific test for lead, except in the presence of bismuth. The dithizone method was used in all of the tests except Nos. 1, 10, 14, and 15.

Comparison standards prepared with vinegar could be used for about 2 hours at most. In this connection, it was found that both test and comparison solutions prepared with acetic acid or citric acid were not satisfactory. The nature of the precipitate imparted a "smoky" color to the solutions and made comparisons difficult or impossible. The condition was corrected by diluting these acids with a 0.25-percent solution of gelatin. Resultant test liquids and standards containing up to 6 parts of Pb per million parts, could be compared satisfactorily. Furthermore, the standards remained constant in color for as much as 2 days.

Copper was determined by "carbamate extraction", using sodium diethyldithiocarbamate, and the procedure followed by the U. S. Bureau of Fisheries.[8] The values are believed to be significant to 0.1 part per million. The following method, giving results significant to 1 part per million, also was used. A 150-ml portion of test solution was evaporated to dryness, ignited, evaporated with $HNO_3$, and treated with 0.5 ml of $NH_4OH$ in a porcelain crucible. The shade of blue obtained was compared with those of standards prepared in the same way.

No test was developed for antimony, because it was evident from results for the yellow glazes that a total of not more than 0.5 part of

[8] E. J. Coulson, J. Assn. Official Agr. Chem. **20**, 178 (1937).

material per million parts of reagent was dissolved by the severest tests.

Blank determinations for lead and for copper indicated that the white vinegar used in the tests (table 1) contained 0.3 and 1.0 part per million, respectively, and that the brown vinegar contained not more than 0.1 part of lead per million parts of vinegar.

## IV. RESULTS AND CONCLUSIONS

The results are presented in figures 1 to 7, inclusive, and some of the values are plotted in several graphs to facilitate comparison and

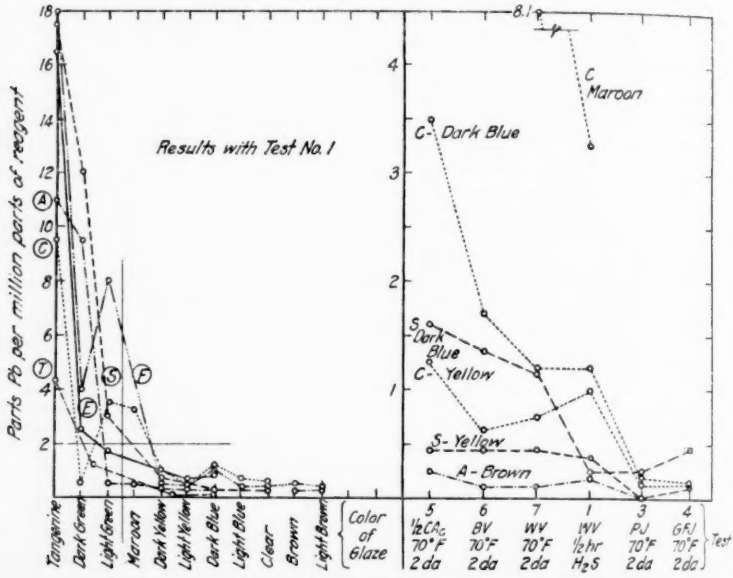


FIGURE 1.—*(Left) effect of test 1 (see table 1) on glazes in 11 colors from 6 manufacturers; (right) effect of tests 3 to 7, inclusive, on glazes of relatively low solubility according to test 1.*

In this figure, as in the others, the letters *A*, *C*, *E*, *F*, *S*, and *T* refer to the manufacturers of the ware tested.

correlation with the various factors involved. Each plot represents the average of at least two determinations, unless otherwise stated.

Data obtained with test 1 on cups in various colors from the cooperating manufacturers are presented in figure 1 (left). Values for some intermediate shades of yellow, brown, blue, and gray (or "white") are omitted, but in no case did they exceed 0.5 part per million. With the exception of one manufacturer's maroon glaze, the only specimens giving up more than 2 parts per million of Pb were the tangerines (reds) and the greens.

Some of the dark blues and yellows showed solubilities equal to or in excess of 1 part per million. These colors, together with the maroon mentioned and a brown, were subjected to tests 3, 4, 5, 6, and 7. The results are shown in figure 1 (right), and values from test 1 are repeated for comparison.

The combined data of figure 1 show that: (a) glazes of high resistance to solution under the conditions of test 1 (not over 1 part per million of Pb) will also present very little, if any, hazard to health, even if "lemonade" (test 5) or distilled vinegar (test 7) is left in contact with them for as much as 2 days; (b) with some colors (for example, dark blue and maroon) contact with vinegar or a citric-acid solution of lemonade strength for 2 days may be dangerously more severe than the tentative test (No. 1) indicates; and (c) the limited time available for this investigation should be concentrated on the tangerine and green glazes.

Accordingly, the specimens of tangerine and green glazes from two concerns were subjected to the series of tests indicated in figure 2.

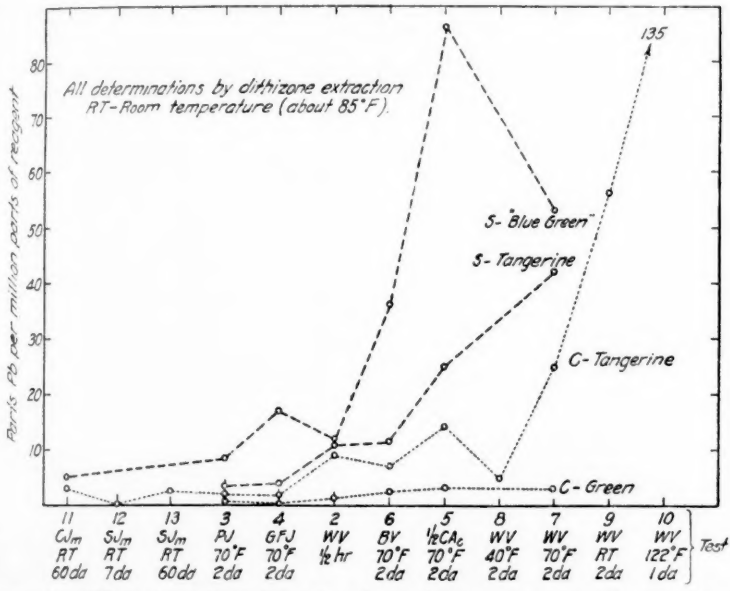


FIGURE 2.—*Effect of accelerated test 2 and simulated service tests 3 to 13, inclusive, on tangerine and green glazes from two manufacturers.*

The first five tests, when reading from left to right, show that their use in the home with fruit juices and jams would be less severe than in laboratory test 2,[9] while tests 6, 5, 7, and 9 (representing home use with lemonade and with vinegar) would be more severe, and the glazes, under these conditions, might be unsafe. For example, a vinegar containing 25 parts of lead per million would have a little over 1 mg of lead in 1.5 fluid ounces. Correspondingly, an 8-ounce tumbler of lemonade would have 6 mg of lead, and in the references cited it was stated that ingesting 1 mg daily produced symptoms.

Tests 8, 7, 9, and 10 were made to show the effect of variation in temperature. They show that vinegar may take up only 5 parts per million during 2 days in a refrigerator but 25 parts in a room when the climate is moderate, and over 50 parts in summer heat. Test 10

[9] Test 2 results were plotted here, instead of test 1, to make the method of analysis common for all tests.

indicates what might be expected if such glazes were used, for example, in warming ovens.

Based on the results described, tests 1, 2, 5, 7, and 16 were selected as representative of both laboratory and service tests. Five tangerine and six green glazes, subjected to these treatments, are represented by the graphs in figure 3. Plotted in the general order of relative severity, the values show first of all that this order is not the same for the two colors, but that more lead is dissolved from green glazes by "lemonade" than is dissolved by white vinegar under the same conditions. Figure 3 shows also, in the large majority of cases and test for test, that the green glazes are more reluctant to give up lead than are the tangerines. The indication of figure 2 that the tentative test (No. 1 or 2) may not be nearly as severe as "home conditions" (Nos. 5 and 7) is substantiated. Also, the substitution of a 0.5-percent citric-acid

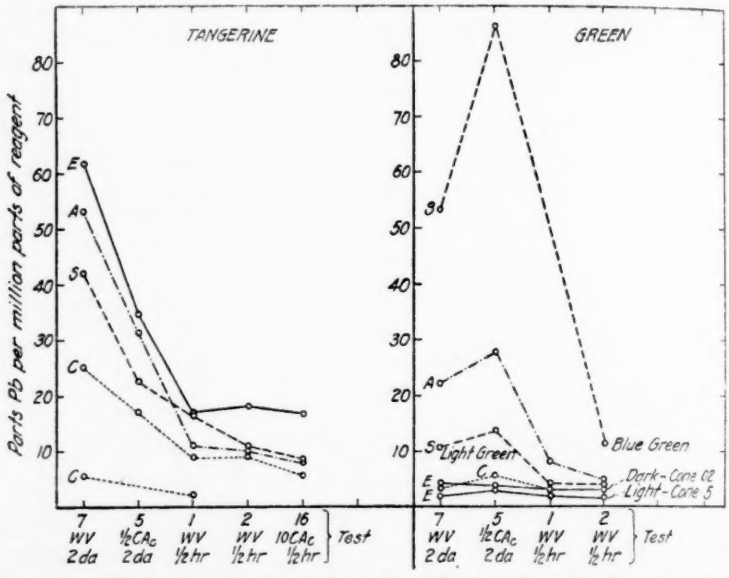


FIGURE 3.—*Effect of accelerated tests 1, 2, and 16 and service tests 5 and 7 on tangerine glazes (left) and on green glazes (right) from four manufacturers.*

solution for distilled 5-percent acetic-acid vinegar in tests 1 and 2 produces roughly comparable results with the tangerine glaze.[10]

Two additional points of interest are brought out by the data in figure 3 (right), namely, the effect of the stain on the solubility of a base glaze and the effect of the glost temperature. The first is illustrated by the graphs for a "blue-green" and a "light-green" glaze. The only known difference between these glazes is that the latter contains only half of the identical stain used in the former. Also, the clear, or "base glaze," to which the stain had been added gave up only 0.6 part per million of lead in test 5. The second point is illustrated by the plots identified as "dark-cone 02" and "light-cone 5." Naturally, the compositions of the two base glazes, and probably

[10] Citric-acid solutions are more desirable than vinegar or acetic-acid solutions for laboratory work, because solutions of known strength can be prepared and maintained more conveniently.

also those of the stains, differed, but the results show that glazing at the lower temperature need not materially lower the resistance to solution.

The possibility of substituting citric-acid solution for vinegar was investigated further, as shown by the information in figure 4. Because of the shortage of cups, test results given in the larger graph were obtained with fruit saucers. They show that differences obtained with tests 1 and 14 are not significant.

Test 16 was then made on tangerine, maroon, and blue cups from one manufacturer to determine the strength of citric acid required in an accelerated test to dissolve glaze comparable to vinegar or lemonade in contact with the glaze for 2 days at 70° F (test 7). The data are plotted in figure 4 (right). Graphs *4C1*, *4C2*, and *4C5* are for three tangerine cups from the fourth shipment. Cups *4C1* and *4C2* were

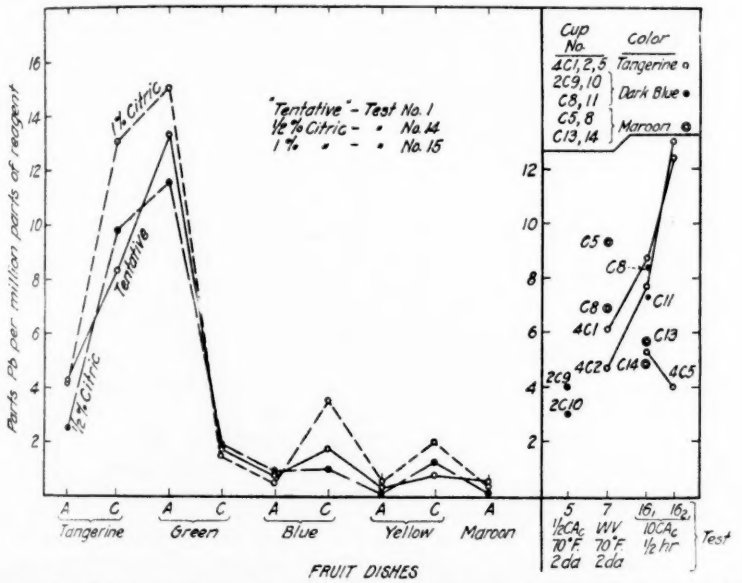


FIGURE 4.—*Relative results with tests 1, 14, and 15 (left) on nine glazes in five colors; and (right) relative results with 10-percent citric-acid solution, test 16, and simulated service tests 5 and 7.*

Test 16 was made twice on cups *4C1* and *4C2*, after having made test 7, and twice on the previously untested cup, *4C5*.

subjected to test 7 and then twice to test 16. Cup *4C5* was subjected twice to test 16. The indication is that a solution containing at least 10 percent of citric acid, when substituted for vinegar in the tentative method in order to obtain values comparable with those of test 5 or 7, will give higher values for some colors (for example, dark blue) and lower values for others (for example, maroon).

The values for individual cups given in figure 4 (right) lead to the question—what variations were found among supposedly duplicate cups? Typical examples are given in table 2. Results with tangerine cups were especially erratic. One of the factors which may be responsible for this is difference in heat treatment. It was thought

this could be illustrated by testing the glaze on the inside and on the outside of several cups. The graphs in figure 5 (left) show that a significant difference is to be found on the same cup, and therefore differences between cups are not surprising.

Another factor to be considered in the testing of commercial ware with a specified amount of reagent (in this case, 150 ml per cup) is the variable surface exposed because of differences in design. Some glazes were represented by the "regular", or approximately hemispherical cup, by a straight-sided cup having the shape of an inverted

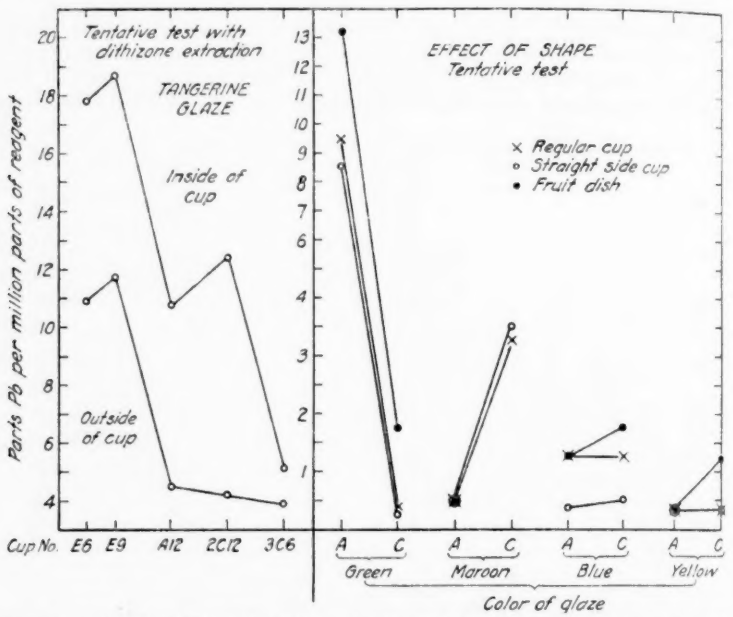
Tentative test with dithizone extraction
TANGERINE GLAZE
Inside of cup
Outside of cup
Parts Pb per million parts of reagent
Cup No. E6 E9 A12 2C12 3C6
EFFECT OF SHAPE
Tentative test
× Regular cup
○ Straight side cup
• Fruit dish
A C A C A C A C
Green Maroon Blue Yellow
Color of glaze

FIGURE 5.—*(Left) relative solubility on inside and on outside of five cups from three manufacturers; (right) effect of shape of specimen (and consequent variation in surface exposed to the 150 ml of reagent) on results with the tentative test 1.*

and truncated cone (frustum), and by fruit dishes. The tentative test (No. 1) was conducted on each shape, using 150 ml of vinegar for each shape. The results (fig. 5, right) show that the greater surface exposed by the fruit dish will usually give slightly higher values for lead dissolved, but the differences introduced by the shapes tested have little significance in the tentative test.

In addition to the above, three bowls in green glaze were subjected to tests 1, 5, and 7, using 325 ml of reagent because the capacity of the bowls was in the ratio of 325:150 to the capacity of comparable cups. The results for cups and for bowls were as follows: Test 1 gave 7 and 8 parts of lead per million; test 5 gave 26.0 and 29.1 parts per million; and test 7 gave 24.5 and 19.0 parts per million, respectively. This shows that similar shapes in various sizes will give comparable results if proportionate amounts of reagent are used.

TABLE 2.—*Variations in solubility among different specimens of the same glaze*

| Manufacturer | Test number | Tangerine | | Yellow | | Green | | Blue | |
|---|---|---|---|---|---|---|---|---|---|
| | | Cup | Lead extracted [a] | Cup | Lead extracted [a] | Cup | Lead extracted [a] | Cup | Lead extracted [a] |
| C | 1 | *C1* [b] | 12 | *C6* | 1 | *C1* | 0.5 | *C6* | 1.5 |
| C | 1 | *3C1* [b] | 12 | *C7* | 1 | *C2* | <0.5 | *C7* | 1.0 |
| C | 1 | *3C3* | 9 | *2C11* | 1 | *2C11* | >3 | *2C12* | 1.0 |
| C | 1 | *3C6* | 6 | *2C12* | 1 | *2C12* | 3 | | |
| C | 2 | *2C11* | 11.1 | | | | | | |
| C | 2 | *2C12* | 12.4 | | | | | | |
| C | 2 | *3C5* | 5.9 | | | | | | |
| C | 2 | *3C6* | 5.1 | | | | | | |
| C | 5 | *2C7* | 13.8 | *2C9* | 0.5 | *2C9* | 5.9 | *2C9* | 4.0 |
| C | 5 | *2C8* | 20.0 | *2C10* | 1.0 | *2C10* | 5.6 | *2C10* | 3.0 |
| A | 1 | *A1* | 11 | *A4* | <0.5 | *A4* | 10 | *A4* | 1.0 |
| A | 1 | *A4* | 9 | *A6* | <0.5 | *A5* | 9 | *A5* | 0.5 |
| A | 1 | *A11* | 12 | | | *A13* | >7 | | |
| A | 2 | *A11* | 11.6 | | | *A6* | 6.0 | | |
| A | 2 | *A12* | 10.0 | | | *A8* | 6.9 | | |
| S | 7 | *S2* | 44.5 | *S2* | 0.5 | *S2* | 48.0 | *S2* | 1.2 |
| S | 7 | *S4* | 40.2 | *S3* | 0.4 | *S3* | 58.0 | *S11* | 1.1 |

[a] Values are in parts of lead (Pb) per million parts of reagent.
[b] The number before the letter indicates the shipment; thus, *3C1* in this column means tangerine cup 1 of the third shipment from manufacturer *C*.

An appreciable difference had been found in the amount of lead indicated by $H_2S$ precipitation, and by dithizone extraction, for some green and also some tangerine glazes. The precipitation of tin might account for the difference in the case of the tangerine glaze. However, the difference was found with a glaze reported as containing only Pb, $Al_2O_3$, $SiO_2$, and $UO_2$—and uranium sulfide is not precipitated in weak acid solutions according to textbooks on the subject. This was checked by passing $H_2S$ through vinegar containing a known amount of uranium. A slight discoloration was produced, much less than that required to account for the differences actually found. Since there is no reason to believe that the slight amounts of uranium which might be ingested would be toxic, the matter was not investigated further.

The case of nausea mentioned in section I, which followed the drinking of tea from a new, green-colored cup may have been caused by copper. It was readily demonstrated that the differences in results for tests 1 and 2 could be explained by the precipitation of CuS. The data given in figure 6 were obtained for four cups, and also for four fruit dishes on each of which test 1 was conducted three times, that is, the acid treatment of test 1 was used, and analytical methods of tests 1 and 2 were made on aliquot portions of the same liquid.

It is evident from figure 6 that the solubility of the green glaze on the fruit dishes, so far as extraction of lead and copper are concerned, had been decreased materially by the first acid treatment. This interesting and important phenomenon was investigated further, and the results are plotted in figure 7. Cups glazed in tangerine, from four manufacturers, were subjected four times to test 1, and duplicate sets were washed with hot water and soap between each test to remove

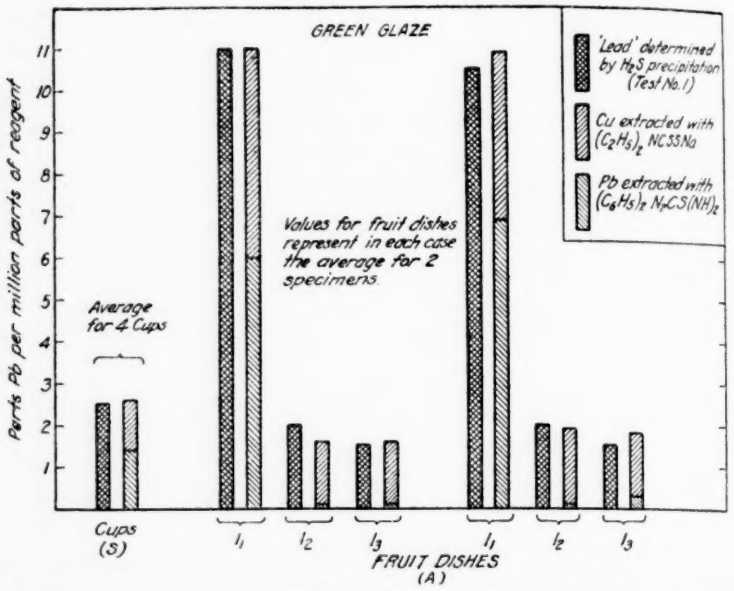
GREEN GLAZE
'Lead' determined by $H_2S$ precipitation (Test No. 1)
Cu extracted with $(C_2H_5)_2$ NCSSNa
Pb extracted with $(C_6H_5)_2$ $N_2CS(NH)_2$
Values for fruit dishes represent in each case the average for 2 specimens.
Average for 4 Cups
Parts Pb per million parts of reagent
Cups (S)
FRUIT DISHES (A)

FIGURE 6.—*Amounts of copper and of lead making up the "lead" dissolved during test 1, as indicated by* $H_2S$ *precipitation.*

The test was made on previously untested cups, and repeated twice on the fruit dishes.

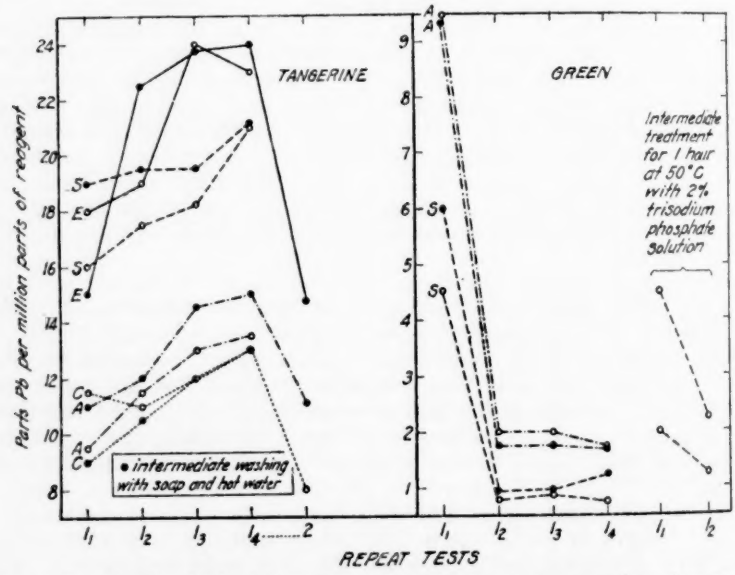
TANGERINE
GREEN
Intermediate treatment for 1 hour at 50°C with 2% trisodium phosphate solution
• intermediate washing with soap and hot water
Parts Pb per million parts of reagent
REPEAT TESTS

FIGURE 7.—*Results obtained by repeating test 1 on tangerine cups from four manufacturers (left) and on green cups from two manufactures.*

One series of cups was permitted to dry in the air between tests, a duplicate series was washed with soap and hot water. Also, the dithizone extraction for Pb (test 2) and the $H_2S$ precipitation was made, on the same solution from the fourth test, for three samples of tangerine glaze.

The intermediate treatment with trisodium phosphate was made to simulate cleansing in a washing machine. The upper and lower pairs of values are on cups of slightly different color from manufacturer S, and from a separate shipment.

any film of colloidal silica which might have formed. Also, in three cases, the dithizone extraction was made, after this fourth test, on an aliquot portion of the same solution. The washing had no marked effect on the solubility. The graphs (fig. 7, left) indicate also that the susceptibility of the tangerine glazes to acid attack will increase with continued use, but that this increase (by the $H_2S$ test) may not, necessarily, mean a proportionate increase in the lead taken up by the acid (dithizone extraction). As mentioned previously, the difference in the amount of dissolved lead, as determined by these two methods, has not been accounted for.

Figure 7 (right) shows the results of four successive tests by method 1 on green glazes from two manufacturers, and again with and without intermediate washing. The first acid treatment has reduced the amount of "lead" extracted ($H_2S$ test) to not over 2 parts per million, supporting the results given in figure 6. It will be recalled that test 1 is a comparatively mild treatment compared with tests 5 and 7. Therefore, these two tests were repeated on two cups (Brand A). For test 5 the lead extracted dropped from 26.0 to 6.5 parts per million; for test 7, from 24.5 to 5.9 parts per million. It was further suggested that a treatment in an alkaline bath, such as ware is subjected to in commercial washing machines, might break down the glaze sufficiently to counteract the effect of the acid wash. Repeat tests were made on cups with an intermediate treatment in 2-percent trisodium phosphate solution at 50° C for 1 hour. The results (fig. 7, right) show that the alkali had little, if any, effect.

## V. DISCUSSION

This discussion deals primarily with the extent to which the results obtained have met the purpose of the work as outlined in section II.

The "tentative test" (No. 1, table 1) appears to be satisfactory with regard to possibility of duplication in different laboratories, as illustrated by the following:

*Case 1.*—A sample of cups tested at the National Bureau of Standards lost 3+, 3−, 2.5, and 2.5 parts of Pb per million parts of reagent, respectively. Cups in a duplicate sample submitted to another laboratory were reported as losing between 2.5 to 3 parts.

*Case 2.*—Average values obtained at the Bureau for four glazes from one manufacturer were: Tangerine 4+, green 1+, yellow $<0.5$, and blue $<0.5$. Values obtained by the manufacturer in the plant laboratory were: $>3$, $>1$, $<0.8$, and $<0.8$, respectively.

That determinations on individual specimens of a sample differ may reasonably be explained by actual differences in the glazes, as shown by the data in figure 5 (left) and by similar differences obtained with the other test methods.

Correlation of results obtained with laboratory tests (Nos. 1, 2, 14, and 15) and those designed to represent conditions in home use (Nos. 3 to 13, incl.) show that the former group of tests adequately determine the lead which might be taken up by fruit juices and jams. They do not, however, give a satisfactory measure of the lead which might be found in weak acid solutions, such as vinegar or lemonade, after 2 days of contact at ordinary temperatures (tests 5 and 7); test 16 was more severe for some colors and less so for others.

The proposed "solubility limit" in the "tentative test" of not over 2 parts of Pb per million parts of reagent should be considered as purely arbitrary until a decision on the matter is made by the proper State or Federal agencies. It is believed desirable, also, to substitute a solution containing 0.5 percent of citric acid and 0.25 percent of gelatin for the white, distilled vinegar (nominally 5-percent acetic acid) at present specified for the tentative test.

The $H_2S$ test for lead and the ammonia test for copper are believed to give values accurate within $\pm 0.5$ part per million for solutions containing not over 6 parts. The $H_2S$ will precipitate also, in weakly acidic solutions, any copper, antimony, or tin which may be present, and this fact must, of course, be taken into consideration when evaluating results. For example, figure 6 shows that the precipitate obtained after the second and third treatments of a typical green glaze was almost entirely copper sulfide.

Whether one glaze will constitute a health hazard and another will not is still a moot question. Nevertheless, it may be said of the typical glazes covered in this investigation that, with one and possibly three exceptions, they very probably will not, provided the manufacturer exercises a modicum of care in their preparation. The first exception is the tangerine glaze from which organic acids extract quantities of lead detrimental to health, as judged by the best available medical records. Furthermore, this condition does not improve with continued use and may actually be aggravated. The two possible exceptions are the dark blue and the maroon, for which values are shown in figure 1. Whether or not these glazes will improve with repeated use was not determined.

Although a green glaze precipitated this study, the results of the investigation indicate that its use is not dangerous under certain conditions. There is reason to believe that the lead and copper dissolved by weak acids from many green glazes as they come from the kiln are a health hazard. Fortunately, this high solubility appears to be a surface condition. The results in figure 6 (which were, incidentally, obtained with the least resistant of the green glazes "in production") show that a preliminary acid wash will reduce the lead absorbed during test 1 to a few tenths of 1 part per million and, probably, to not over 6 parts per million during the severe conditions of tests 5 and 7. This does not seem to warrant much concern, but it would seem preferable to use copper-free stains for the green glazes. These glazes do constitute a potential danger, and every precaution should be exercised to assure their harmlessness to the user.

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# DENSITY OF SOME SODA-POTASH-SILICA GLASSES AS A FUNCTION OF THE COMPOSITION

By John C. Young, Francis W. Glaze, Conrad A. Faick, and Alfred N. Finn

ABSTRACT

Certain relations between the specific volume and composition of glasses of the soda-silica series have previously been reported. Additional glasses were made in the same series and also in the potash-silica and soda-potash-silica series. The glasses were analyzed and their densities measured. Analysis of the new data suggests that the specific volume-composition relations change definitely at compositions approximating those of eutectics, instead of at those of simple molecular ratios, as previously reported.

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## I. INTRODUCTION

The densities of 37 soda-silica glasses, containing from 13 to 50 percent of soda, were reported in a previous publication [1],[1] and certain relations between specific volume and composition were suggested. Since those data were published, many new glasses in the same range of composition have been made. These, together with all of the former glasses still available for further experimentation, constitute a new series of 50 soda-silica glasses whose densities and compositions are given in the present report. This report also includes data on 66 potash-silica glasses varying in composition from 17 to 40 percent of potash, and on 78 soda-potash-silica glasses whose compositions were distributed throughout the field between the composition-ranges of the two binary series. All the glasses were given the same heat treatment, which treatment differed materially from that described in the earlier report.

Study of the new data, which are considerably more numerous as well as more reproducible than those previously reported, indicated the desirability of some revision of the conclusions based on the previous data. In addition to presenting the new data, therefore, the present paper replaces that part of the earlier one which dealt with the soda-silica glasses.

[1] Figures in brackets indicate the literature references at the end of this paper.

## II. PREPARATION OF THE GLASSES

The reader is referred to previous publications [1, 2] for a description of the methods of preparation and analysis, and determination of density of the glasses.

"Weathering" of some of the soda-silica glasses remaining from the original series was found to have occurred when these specimens were examined for inclusion in the new series. This weathering appeared to be merely a surface effect, however, and in each case tried the original density of the glass was restored (which implied that the "interior composition" had not been changed) by removal of the surface to a depth of about 1 mm by grinding with carborundum and water. The use of water proved satisfactory provided the glasses were dried immediately after grinding. For most of the glasses the procedure was to grind off the surface twice or more immediately following heat treatment, measuring the density after each grinding, until no further change in density was noted. The densities of the few glasses which had been "reconditioned" by grinding before heat treatment were measured directly after heat treatment. These densities remained unchanged by subsequent grinding.

## III. HEAT TREATMENT

In the previously reported work, each glass was held for an hour at approximately its highest "annealing temperature." Subsequent experience indicates, however, that insufficient knowledge and control of the rates of cooling from these temperatures had introduced errors which would hinder a satisfactory evaluation of the data. In an effort, therefore, to develop a method for giving reproducible and "comparable"[2] heat treatments, five different heat treatments were applied successively to each of 11 glasses (indicated by the symbol ⊙ in figure 4) representative of the entire field of compositions studied. The heat treatments (represented schematically) and the densities after each treatment (tabulated directly beneath the respective schematic curves) are given in figure 1 in the order in which the heat treatments were applied.

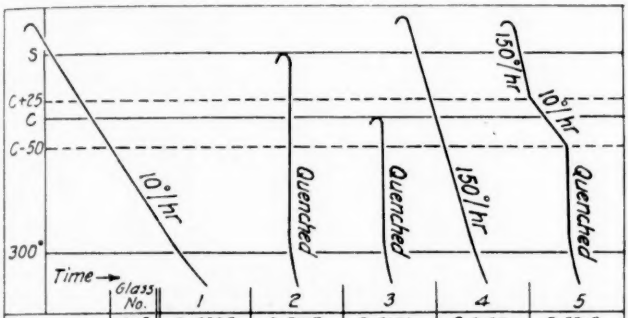
### 1. DEVELOPMENT OF FIGURE 1

The "critical temperatures" and "softening temperatures" were determined for each glass as described in a former paper [11]. The term "critical range", as used herein, may be defined as a temperature interval (for each glass) above and below which large variations in cooling rate did not appreciably affect the final, or room temperature, density. An indication of the practical limits of this range is given below in the discussion of results of heat-treating experiments.

In treatments 2, 3, and 5 the glasses were necessarily treated individually since the critical temperature, softening point, and critical range are different for each glass. The difficulties involved in the individual treatments are, however, such that the results obtained are merely indicative. First, the various critical temperatures, etc., cannot be determined with assurance; and second, the extreme nature of the quenching process is such that no single experiment could be repeated in every detail. For treatment 1, however, in which it was

[2] The word "comparable", as used here, is intended to convey the idea of a common basis for comparison of the densities of glasses of different compositions so far as the densities may be affected by differences in heat treatment.

desired to maintain the cooling rate constant, and the same for all glasses, not only through the respective critical ranges but also for a considerable temperature interval on either side, these two difficulties were largely obviated by cooling all the glasses simultaneously in a furnace whose cooling rate was essentially constant through a temperature interval (550° to 300° C), which included by a fairly wide margin the critical range of every glass to be treated. For treatment 4 the glasses were similarly treated except that a different furnace (one having a much greater cooling rate) was used. All glasses made for this investigation were given treatment 1, whereas the 11 glasses for which data are given in figure 1 and, in addition, 14 soda-silica, 12 potash-silica, and 7 soda-potash-silica glasses were selected for treat-




| | Glass No. | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|---|
| Densities resulting from each treatment | 302 | 2.5205 | 2.5167 | 2.5181 | 2.5178 | 2.5215 |
| | 317 | 2.3435 | 2.3379 | 2.3407 | 2.3407 | 2.3429 |
| | 319 | 2.5047 | 2.4982 | 2.5044 | 2.4990 | 2.5050 |
| | 330 | 2.4868 | 2.4827 | 2.4869 | 2.4833 | 2.4857 |
| | 336 | 2.4502 | 2.4458 | 2.4473 | 2.4460 | 2.4498 |
| | 346 | 2.4469 | 2.4429 | 2.4451 | 2.4445 | 2.4471 |
| Treatments applied consecutively to the same specimen of each glass | 356 | 2.4111 | 2.4084 | 2.4092 | 2.4084 | 2.4116 |
| | 363 | 2.4348 | 2.4299 | 2.4330 | 2.4303 | 2.4346 |
| | 367 | 2.4066 | 2.4005 | 2.4055 | 2.4028 | 2.4066 |
| | 371 | 2.3935 | 2.3866 | 2.3907 | 2.3899 | 2.3932 |
| | 377 | 2.3227 | 2.3205 | 2.3228 | 2.3200 | 2.3225 |

FIGURE 1.—*Schematic cooling curves for each of the 11 glasses, with densities resulting from each treatment shown at the base of the corresponding curve.*

*S*, softening temperature—different for each glass; *C*, critical temperature—different for each glass. The curves are not drawn to scale.

ment 4. Complete density data for these two treatments are included in table 1.

It is noteworthy that the density of a specimen after treatment does not depend upon the size of the specimen, providing size, as such, is not a factor in determining the rate of cooling (as, for instance, when the specimen is quenched in air). For example, it was found that a 46-g block of borosilicate crown glass (density approximately 2.51) and some small chips of the same material, each chip weighing about 0.2 g, had within experimental limits the same density after having been cooled simultaneously at about 70° C per hour from above the critical range. The density of the chips was measured as a composite sample. When the same specimens were quenched in air from the temperature just indicated, the large block had a considerably greater density ($\Delta$=0.0050) than the small chips, the "free" cooling rate of the former necessarily being much less than those of the chips.

TABLE 1.—*Density and composition for 194 soda-potash-silica glasses*

| Glass number[1] | Composition | | | Density | | Glass number[1] | Composition | | | Density | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Na_2O$ | $K_2O$ | Treatment 1 | Treatment 4 | | $SiO_2$ | $Na_2O$ | $K_2O$ | Treatment 1 | Treatment 4 |
| | % | % | % | | | | % | % | % | | |
| 1 (3) | 51.62 | 48.38 | ..... | 2.5676 | ..... | 211 | 68.10 | ..... | 31.90 | 2.4131 | 2.4079 |
| 2 (4) | 52.60 | 47.40 | ..... | 2.5622 | ..... | 212 | 68.60 | ..... | 31.40 | 2.4108 | ..... |
| 3 (5) | 53.62 | 46.38 | ..... | 2.5557 | ..... | 213 | 68.86 | ..... | 31.14 | 2.4086 | ..... |
| 4 (8) | 57.45 | 42.55 | ..... | 2.5361 | 2.5325 | 214 | 69.17 | ..... | 30.83 | 2.4074 | ..... |
| 5 (9) | 58.98 | 41.02 | ..... | 2.5286 | 2.5254 | 215 | 69.32 | ..... | 30.68 | 2.4064 | ..... |
| 6 | 59.04 | 40.96 | ..... | 2.5290 | ..... | 216 | 69.50 | ..... | 30.50 | 2.4046 | ..... |
| 7 (10) | 59.69 | 40.31 | ..... | 2.5262 | ..... | 217 | 69.77 | ..... | 30.23 | 2.4047 | ..... |
| 8 (11) | 59.71 | 40.29 | ..... | 2.5257 | ..... | 218 | 70.11 | ..... | 29.89 | 2.4015 | ..... |
| 9 (12) | 59.97 | 40.03 | ..... | 2.5236 | ..... | 219 | 70.35 | ..... | 29.65 | 2.3994 | ..... |
| 10 | 61.17 | 38.83 | ..... | 2.5168 | ..... | 220 | 70.58 | ..... | 29.42 | 2.3984 | ..... |
| 11 | 61.77 | 38.23 | ..... | 2.5147 | ..... | 221 | 70.64 | ..... | 29.36 | 2.3972 | ..... |
| 12 | 62.58 | 37.42 | ..... | 2.5111 | ..... | 222 | 70.93 | ..... | 29.07 | 2.3966 | ..... |
| 13 (13) | 62.77 | 37.23 | ..... | 2.5092 | 2.5053 | 223 | 71.35 | ..... | 28.65 | 2.3927 | ..... |
| 14 | 62.78 | 37.22 | ..... | 2.5094 | ..... | 224 | 71.45 | ..... | 28.55 | 2.3940 | ..... |
| 15 (14) | 62.86 | 37.14 | ..... | 2.5084 | ..... | 225 | 71.65 | ..... | 28.35 | 2.3929 | ..... |
| 16 (15) | 63.06 | 36.94 | ..... | 2.5079 | ..... | 226 | 71.67 | ..... | 28.33 | 2.3923 | 2.3884 |
| 17 | 63.13 | 36.87 | ..... | 2.5080 | ..... | 227 | 71.68 | ..... | 28.32 | 2.3928 | ..... |
| 18 | 63.60 | 36.40 | ..... | 2.5056 | ..... | 228 | 72.26 | ..... | 27.74 | 2.3888 | ..... |
| 19 | 64.00 | 36.00 | ..... | 2.5028 | ..... | 229 | 72.30 | ..... | 27.70 | 2.3884 | ..... |
| 20 | 64.71 | 35.29 | ..... | 2.4979 | ..... | 230 | 72.33 | ..... | 27.67 | 2.3891 | ..... |
| 21 (17) | 65.32 | 34.68 | ..... | 2.4961 | 2.4925 | 231 | 72.45 | ..... | 27.55 | 2.3886 | ..... |
| 22 | 65.72 | 34.28 | ..... | 2.4912 | ..... | 232 | 72.49 | ..... | 27.51 | 2.3874 | ..... |
| 23 | 66.16 | 33.84 | ..... | 2.4904 | ..... | 233 | 72.60 | ..... | 27.40 | 2.3868 | ..... |
| 24 (18) | 66.52 | 33.48 | ..... | 2.4869 | ..... | 234 | 72.74 | ..... | 27.26 | 2.3862 | ..... |
| 25 | 66.58 | 33.42 | ..... | 2.4859 | ..... | 235 | 73.00 | ..... | 27.00 | 2.3850 | ..... |
| 26 | 67.07 | 32.93 | ..... | 2.4830 | ..... | 236 | 73.14 | ..... | 26.86 | 2.3840 | ..... |
| 27 | 67.22 | 32.78 | ..... | 2.4821 | ..... | 237 | 73.15 | ..... | 26.85 | 2.3828 | ..... |
| 28 | 67.35 | 32.65 | ..... | 2.4816 | ..... | 238 | 73.25 | ..... | 26.75 | 2.3830 | ..... |
| 29 | 68.10 | 31.90 | ..... | 2.4770 | ..... | 239 | 73.45 | ..... | 26.55 | 2.3815 | ..... |
| 30 | 68.81 | 31.19 | ..... | 2.4722 | 2.4692 | 240 | 73.63 | ..... | 26.37 | 2.3807 | ..... |
| 31 | 69.10 | 30.90 | ..... | 2.4706 | ..... | 241 | 73.67 | ..... | 26.33 | 2.3812 | 2.3767 |
| 32 (20) | 69.65 | 30.35 | ..... | 2.4670 | 2.4645 | 242 | 74.15 | ..... | 25.85 | 2.3781 | ..... |
| 33 (22) | 70.44 | 29.56 | ..... | 2.4623 | ..... | 243 | 74.37 | ..... | 25.63 | 2.3756 | ..... |
| 34 | 71.10 | 28.90 | ..... | 2.4571 | 2.4540 | 244 | 74.89 | ..... | 25.11 | 2.3728 | 2.3693 |
| 35 (23) | 72.15 | 27.85 | ..... | 2.4519 | ..... | 245 | 74.99 | ..... | 25.01 | 2.3734 | ..... |
| 36 (24) | 72.33 | 27.67 | ..... | 2.4505 | ..... | 246 | 75.00 | ..... | 25.00 | 2.3728 | 2.3692 |
| 37 | 73.00 | 27.00 | ..... | 2.4450 | 2.4420 | 247 | 75.32 | ..... | 24.68 | 2.3721 | ..... |
| 38 | 73.92 | 26.08 | ..... | 2.4387 | ..... | 248 | 75.49 | ..... | 24.51 | 2.3701 | ..... |
| 39 (25) | 74.16 | 25.84 | ..... | 2.4378 | ..... | 249 | 75.76 | ..... | 24.24 | 2.3691 | ..... |
| 40 (26) | 74.69 | 25.31 | ..... | 2.4356 | 2.4332 | 250 | 76.34 | ..... | 23.66 | 2.3646 | ..... |
| 41 (27) | 75.20 | 24.71 | ..... | 2.4289 | 2.4261 | 251 | 76.46 | ..... | 23.54 | 2.3629 | ..... |
| 42 (28) | 76.60 | 23.40 | ..... | 2.4152 | 2.4126 | 252 | 76.57 | ..... | 23.43 | 2.3636 | ..... |
| 43 (29) | 76.65 | 23.35 | ..... | 2.4152 | 2.4133 | 253 | 76.65 | ..... | 23.35 | 2.3625 | ..... |
| 44 (30) | 76.70 | 23.30 | ..... | 2.4141 | ..... | 254 | 76.82 | ..... | 23.18 | 2.3595 | ..... |
| 45 (31) | 77.85 | 22.15 | ..... | 2.4031 | 2.4013 | 255 | 77.27 | ..... | 22.73 | 2.3579 | ..... |
| 46 (32) | 78.61 | 21.39 | ..... | 2.3945 | ..... | 256 | 77.74 | ..... | 22.26 | 2.3529 | 2.3499 |
| 47 | 81.54 | 18.46 | ..... | 2.3677 | ..... | 257 | 77.93 | ..... | 22.07 | 2.3523 | ..... |
| 48 | 82.72 | 17.28 | ..... | 2.3553 | ..... | 258 | 78.74 | ..... | 21.26 | 2.3470 | ..... |
| 49 (36) | 85.15 | 14.85 | ..... | 2.3329 | 2.3310 | 259 | 79.08 | ..... | 20.92 | 2.3450 | 2.3414 |
| 50 | 86.12 | 13.88 | ..... | 2.3230 | ..... | 260 | 79.22 | ..... | 20.78 | 2.3430 | ..... |
| (38) | 100 | ..... | ..... | 2.203 | ..... | 261 | 80.02 | ..... | 19.98 | 2.3366 | 2.3339 |
| 201 | 60.59 | ..... | 39.41 | 2.4522 | ..... | 262 | 80.58 | ..... | 19.42 | 2.3336 | ..... |
| 202 | 60.81 | ..... | 39.19 | 2.4481 | ..... | 263 | 80.99 | ..... | 19.01 | 2.3303 | 2.3277 |
| 203 | 60.88 | ..... | 39.12 | 2.4489 | 2.4433 | 264 | 81.00 | ..... | 19.00 | 2.3314 | ..... |
| 204 | 61.90 | ..... | 38.10 | 2.4449 | ..... | 265 | 82.87 | ..... | 17.13 | 2.3178 | ..... |
| 205 | 62.93 | ..... | 37.07 | 2.4383 | 2.4326 | 266 | 82.99 | ..... | 17.01 | 2.3172 | ..... |
| 206 | 63.93 | ..... | 36.07 | 2.4347 | ..... | 301 | 60.14 | 34.75 | 5.11 | 2.5198 | ..... |
| 207 | 65.08 | ..... | 34.92 | 2.4279 | ..... | 302 | 60.43 | 37.06 | 2.51 | 2.5205 | 2.5178 |
| 208 | 65.92 | ..... | 34.08 | 2.4242 | 2.4196 | 303 | 60.53 | 25.09 | 14.38 | 2.5117 | ..... |
| 209 | 67.02 | ..... | 32.98 | 2.4185 | ..... | 304 | 61.62 | 29.81 | 8.57 | 2.5097 | ..... |
| 210 | 67.24 | ..... | 32.76 | 2.4166 | ..... | | | | | | |

[1] Figures in parentheses are the numbers of the same glasses in the earlier density paper.

TABLE 1.—*Density and composition for 194 soda-potash-silica glasses*—Continued

| Glass number | Composition | | | Density | | Glass number | Composition | | | Density | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Na_2O$ | $K_2O$ | Treatment 1 | Treatment 4 | | $SiO_2$ | $Na_2O$ | $K_2O$ | Treatment 1 | Treatment 4 |
| | % | % | % | | | | % | % | % | | |
| 305 | 62.89 | 35.85 | 1.26 | 2.5084 | ..... | 342 | 70.61 | 15.18 | 14.21 | 2.4409 | ..... |
| 306 | 62.99 | 27.00 | 10.01 | 2.5004 | ..... | 343 | 70.60 | 12.90 | 16.50 | 2.4348 | ..... |
| 307 | 63.48 | 32.78 | 3.74 | 2.5044 | ..... | 344 | 70.76 | 20.03 | 9.21 | 2.4464 | ..... |
| 308 | 64.89 | 33.56 | 1.55 | 2.4968 | ..... | | | | | | |
| 309 | 65.42 | 28.38 | 6.20 | 2.4911 | ..... | 345 | 70.87 | 10.04 | 19.09 | 2.4301 | ..... |
| | | | | | | 346 | 72.30 | 25.20 | 2.50 | 2.4469 | 2.4445 |
| 310 | 66.00 | 30.84 | 3.12 | 2.4886 | ..... | 347 | 71.75 | 7.04 | 21.21 | 2.4191 | ..... |
| 311 | 68.32 | 27.70 | 3.98 | 2.4740 | 2.4706 | 348 | 72.77 | 10.45 | 16.78 | 2.4176 | ..... |
| 312 | 68.33 | 29.85 | 1.82 | 2.4741 | ..... | 349 | 72.92 | 15.27 | 11.81 | 2.4268 | ..... |
| 313 | 71.20 | 27.50 | 1.29 | 2.4564 | ..... | | | | | | |
| 314 | 77.19 | 21.08 | 1.73 | 2.4087 | ..... | 350 | 73.28 | 12.69 | 14.03 | 2.4181 | ..... |
| | | | | | | 351 | 73.66 | 7.51 | 18.83 | 2.4050 | ..... |
| 315 | 80.61 | 10.13 | 9.26 | 2.3630 | ..... | 352 | 73.60 | 22.55 | 3.85 | 2.4360 | ..... |
| 316 | 80.58 | 14.99 | 4.43 | 2.3706 | ..... | 353 | 73.90 | 16.63 | 9.47 | 2.4218 | ..... |
| 317 | 83.43 | 12.00 | 4.58 | 2.3435 | 2.3407 | 354 | 74.76 | 23.99 | 1.25 | 2.4312 | ..... |
| 318 | 84.52 | 8.66 | 6.82 | 2.3275 | 2.3253 | | | | | | |
| 319 | 59.31 | 16.97 | 23.72 | 2.5047 | 2.4990 | 355 | 75.12 | 12.57 | 12.31 | 2.4048 | ..... |
| | | | | | | 356 | 75.38 | 14.80 | 9.82 | 2.4111 | 2.4084 |
| 320 | 60.51 | 20.24 | 19.25 | 2.5048 | ..... | 357 | 75.52 | 7.75 | 16.73 | 2.3943 | 2.3912 |
| 321 | 60.73 | 15.12 | 24.15 | 2.4926 | ..... | 358 | 75.87 | 10.21 | 13.92 | 2.3968 | ..... |
| 322 | 61.12 | 10.27 | 28.61 | 2.4825 | ..... | 359 | 76.30 | 16.79 | 6.91 | 2.4063 | ..... |
| 323 | 61.41 | 12.00 | 26.59 | 2.4837 | ..... | | | | | | |
| 324 | 62.33 | 22.83 | 14.84 | 2.4982 | ..... | 360 | 78.94 | 9.27 | 11.79 | 2.3764 | ..... |
| | | | | | | 361 | 61.54 | 5.04 | 33.42 | 2.4653 | ..... |
| 325 | 62.62 | 7.61 | 29.77 | 2.4685 | ..... | 362 | 64.14 | 2.09 | 33.77 | 2.4422 | ..... |
| 326 | 62.90 | 15.85 | 21.25 | 2.4826 | ..... | 363 | 66.44 | 3.30 | 30.26 | 2.4348 | 2.4303 |
| 327 | 63.70 | 12.69 | 23.61 | 2.4726 | ..... | 364 | 68.73 | 4.40 | 26.87 | 2.4258 | ..... |
| 328 | 64.78 | 17.21 | 18.01 | 2.4757 | ..... | | | | | | |
| 329 | 65.08 | 15.39 | 19.53 | 2.4700 | ..... | 365 | 69.11 | 1.54 | 29.35 | 2.4140 | ..... |
| | | | | | | 366 | 70.75 | 5.25 | 24.00 | 2.4191 | ..... |
| 330 | 65.23 | 24.86 | 9.91 | 2.4868 | 2.4833 | 367 | 71.00 | 2.55 | 26.45 | 2.4066 | 2.4028 |
| 331 | 65.25 | 8.55 | 26.20 | 2.4542 | ..... | 368 | 71.28 | 0.96 | 27.76 | 2.3999 | ..... |
| 332 | 65.37 | 20.10 | 14.53 | 2.4775 | ..... | 369 | 71.61 | 5.35 | 23.04 | 2.4145 | ..... |
| 333 | 65.82 | 10.08 | 24.10 | 2.4572 | ..... | | | | | | |
| 334 | 66.50 | 13.00 | 20.50 | 2.4591 | ..... | 370 | 73.50 | 2.19 | 24.31 | 2.3898 | ..... |
| | | | | | | 371 | 74.35 | 4.44 | 21.21 | 2.3935 | 2.3899 |
| 335 | 66.97 | 21.80 | 11.23 | 2.4700 | ..... | 372 | 75.48 | 3.37 | 21.15 | 2.3797 | 2.3764 |
| 336 | 67.43 | 12.09 | 20.48 | 2.4502 | 2.4460 | 373 | 75.62 | 5.12 | 19.26 | 2.3851 | ..... |
| 337 | 67.92 | 10.01 | 22.07 | 2.4436 | ..... | 374 | 76.05 | 1.03 | 22.92 | 2.3696 | ..... |
| 338 | 68.02 | 15.09 | 16.89 | 2.4544 | ..... | | | | | | |
| 339 | 68.12 | 6.93 | 24.95 | 2.4384 | 2.4337 | 375 | 79.30 | 4.55 | 16.15 | 2.3581 | ..... |
| | | | | | | 376 | 81.05 | 5.24 | 13.71 | 2.3467 | 2.3443 |
| 340 | 69.98 | 24.60 | 5.42 | 2.4603 | 2.4573 | 377 | 83.17 | 2.16 | 14.67 | 2.3227 | 2.3200 |
| 341 | 69.94 | 8.08 | 21.98 | 2.4300 | ..... | 378 | 84.69 | 5.27 | 10.04 | 2.3197 | ..... |

The size of the specimen does, however, affect the accuracy to which the density may be measured. In general, the sizes of the specimens were such that the experimental error in density varied from about $\pm 0.0002$ to $\pm 0.0004$. The 11 specimens used in the several heat-treating experiments, however, were so selected as to be of nearly the same size, in order that the results of the quenching experiments might be comparable.

## 2. RESULTS OF HEAT-TREATING EXPERIMENTS

It will be noted that for any given glass the two densities resulting from treatments 1 and 5, respectively, are essentially the same, although the cooling rates were alike only through a temperature interval between approximately 25° C above to 50° C below the critical temperature. It may be said, therefore, that this interval includes the critical range as defined above. Although no attempt was made to determine the limits for this range more closely, it is interesting to note that a considerable increase in the density of a given glass over that found by quenching from the softening temperature (treatment 2) was

obtained merely by heating the glass rapidly to the critical temperature and immediately quenching it in air (treatment 3). In 3 of the 11 cases, the densities increased enough to equal those resulting from treatment 1.

From a comparison of the results of treatments 4 and 1, respectively, it was found that the difference between the corresponding specific volumes ($V_4$ and $V_1$) is a linear function of the percentages of soda ($B$) and potash ($E$) (no serious error was introduced in assuming the factor for silica ($A$) to be zero). Specifically, for each glass

$$V_4 - V_1 = (1.6B + 2.5E) \times 10^{-5}$$

The individual deviations from this expression were found not to exceed the errors incident to the measurement of specific volume.[3] Thus, it follows (provided the cooling rate is constant, and the same for all the glasses, through their respective critical ranges) that the actual rate used does not determine the character of the surface showing the relationship between specific volume and composition, nor establish the existence or location of "critical points" such as those noted in the following sections. For if

$$V_1 = f_1(A,B,E),$$

then

$$V_4 = f_1(A,B,E) + (1.6B + 2.5E) \times 10^{-5},$$

and at any given composition the rate of change of slope is the same for both surfaces, as the second derivatives are identical. Since the two cooling rates used are wholly arbitrary, it is reasonable to infer that a similar relation would hold had some other rates been chosen.

For the purpose of correlating specific volume with composition, the specific volumes used were those resulting from treatment 1.[4]

## IV. EVALUATION OF THE DATA

In figure 2, specific volume, $V$ ($=1/D$), is plotted as a function of silica content for the potash-silica ($A$) and soda-silica glasses ($B$), as well as for a short series of lithia-silica glasses ($C$) discussed in the next section. For a closer study of these data, in order to determine the type of function which would best represent them, the points were replotted as in figure 3, the ordinates ($\Delta V$) representing, for each binary series, the departures of the observed $V$-values from the respective straight lines $a$ and $b$, indicated in figure 2.

[3] Specific volume is, of course, determined from the same measurements as density—weight and volume. In figure 1, and also in table 1, density, being the more familiar quantity, is recorded rather than specific volume.

[4] The densities of the soda-silica glasses reported by Morey and Merwin [3], which were "annealed to maximal density", correspond very closely to those obtained from treatment 1, except in the very low soda range of composition. In this range the densities of our glasses were lower. After table 1 was prepared, the 14 soda-silica glasses used in treatment 4 (see table 1) were re-treated by the same procedure, except that a cooling rate of about 2° per hour was used. The resulting densities were as follows:

| | | | | |
|---|---|---|---|---|
| (4) Devitrified. | (21) 2.4992. | (34) 2.4587. | (41) 2.4307. | (45) 2.4059. |
| (5) 2.5312. | (30) 2.4752. | (37) 2.4468. | (42) 2.4168. | (49) 2.3336. |
| (13) 2.5120. | (32) 2.4697. | (40) 2.4381. | (43) 2.4179. | |

As was expected, these densities are greater than those resulting from treatment 1. The new densities, although remaining lower than those of Morey and Merwin for glasses containing less than about 23 percent of soda, were somewhat higher than theirs (in the order of about 0.003) for glasses containing more than about 27 percent of soda.

Certainly none of the simpler types of curves would be adequate for representing these data since, from figure 3, the best fit appears to be provided for each series by a line undergoing a "deflection" (that is, a rapid, although perhaps "continuous," alteration in direction) through each of two narrow ranges of composition, while remaining relatively straight outside these ranges.[5] For the purpose of simplicity in expressing this fact mathematically, it was decided that three straight lines could be fitted to the points of each binary series, the intersections

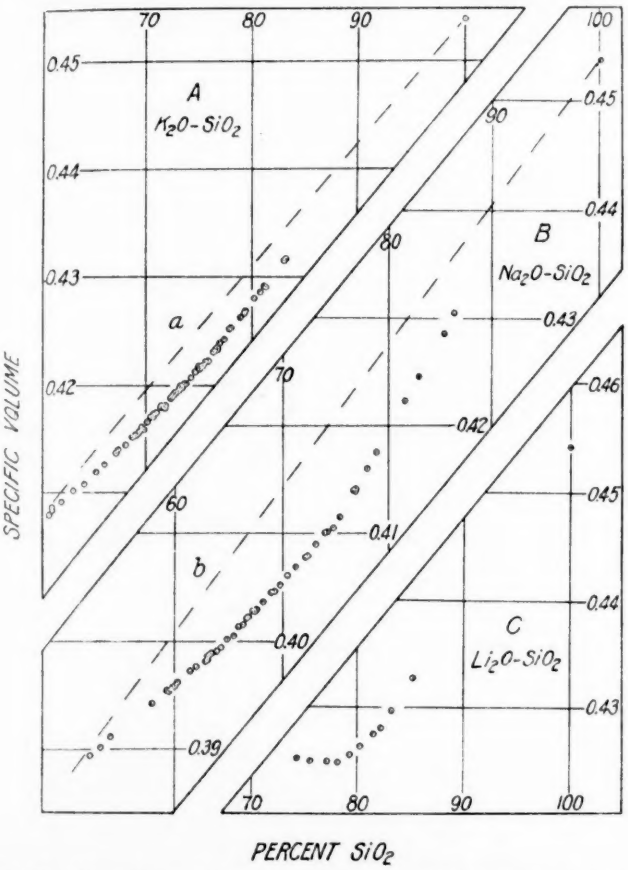



FIGURE 2.—*Specific volume of A the potash-silica, B the soda-silica, and C the lithia-silica glasses plotted against the percentage of silica.*

of these lines representing the deflections in the "true" function—in whatever way that function should "properly" be expressed.

The dashed lines in figure 3 for each series represent the maximum expected deviation on either side of the "best-fitting" straight lines (the constants of which were evaluated as part of the correlation of the ternary relations described below), taking into account only the esti-

[5] In the previously mentioned report by Morey and Merwin the "smooth curve," which they have drawn through their density-composition (and also their refractive index-composition) points, exhibits similar characteristics—a fact made sharply evident by plotting the first derivative of their curve.

mated maximum error in making the chemical analyses (expressible as $\pm 0.2$ percent $SiO_2$), and in the measurement of specific volume ($\pm 0.0001$). The fact that only three or four points in each series lie outside these limits is further indication that the method of heat treatment is reproducible.

To determine the relation between specific volume and composition of the soda-potash-silica glasses, their compositions were plotted on a triordinate diagram (fig. 4). Then several lines of constant V

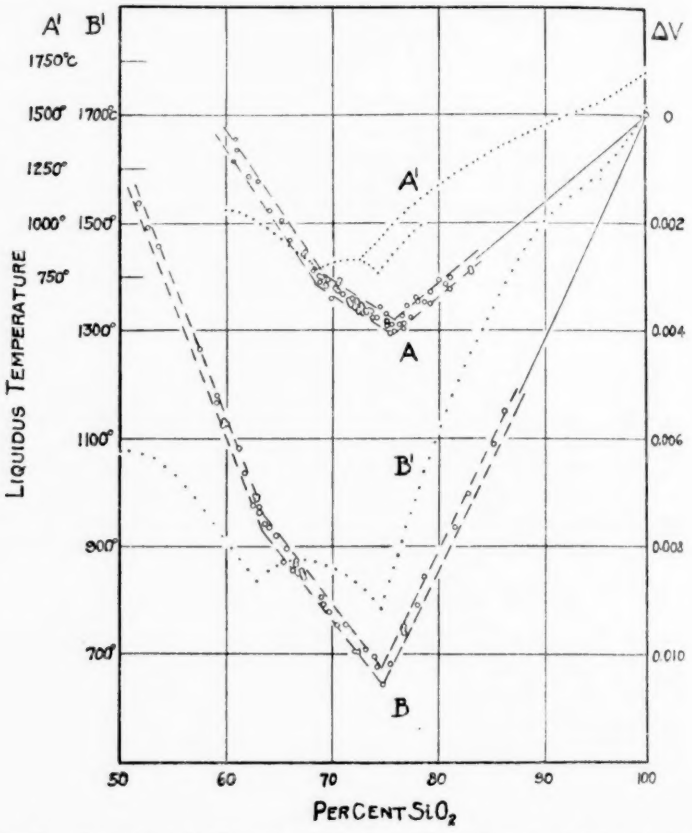



FIGURE 3.—*Departures* ($\Delta V$) *of the observed specific volumes of A the potash-silica, and B the soda-silica glasses from the corresponding straight lines a and b in figure 2.*

*A'* and *B'* are the corresponding liquidus curves, taken from references [3] and [4].

(specific volume) were obtained by first interpolating graphically each selected constant $V$ value between several appropriate pairs of neighboring points, and then sketching a smooth line through each of the sets of interpolated points representing the same $V$ value. The trend and separation of the constant $V$ lines thus drawn revealed that the over-all surface, representing the variation in specific volume with composition, divided itself into several relatively flat regions of different slopes. Accordingly, each region was treated arbitrarily as a

plane of the form $V=aA+bB+eE$, in which $A$, $B$, and $E$ are the percentages of silica, soda, and potash, respectively, and $a$, $b$, and $e$ are constants which are different for each region. The constants were evaluated for each region by the method of least squares, using the foregoing graphic representation as a guide for the appropriate grouping of the points. The data for the two binary series were, of course, also included in these calculations, but the points are not recorded on the triordinate diagrams. The constants thus derived are shown in table 2 and are given to $5\times10^{-7}$ in order to avoid numerical errors in the "computed specific volumes" as great as the error in measuring

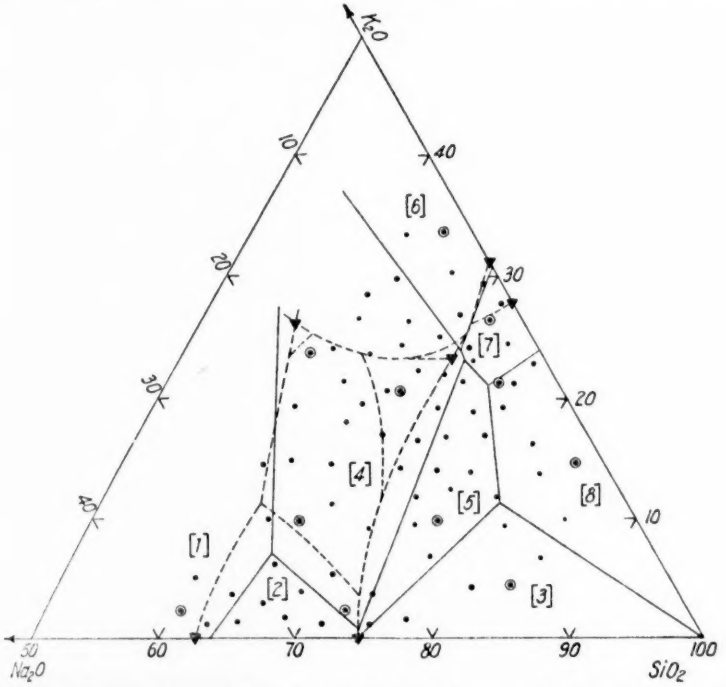



FIGURE 4.—*Compositions of the soda-potash-silica glasses and the boundaries (solid lines) of the various planes (numbered as in table 2) representing the surface on which the specific volumes lie.*

Dotted lines are the boundary curves of the phase-equilibrium diagram. Points in circles identify the glasses used in the heat-treating experiments outlined in figure 1.

specific volume. The statistical error in the constants themselves is, of course, much greater than $5\times10^{-7}$.

Simultaneous solutions, by pairs, of the equations of adjacent planes yielded the lines of intersection of the planes (shown by heavy lines, fig. 4).

TABLE 2.—*Numerical value of constants for the different regions*

| Constant×100 | Region→1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
|---|---|---|---|---|---|---|---|---|
| a | 0.428 00 | 0.437 10 | 0.454 00 | 0.441 05 | 0.448 35 | 0.441 65 | 0.447 85 | 0.454 00 |
| b | .348 60 | .332 65 | .282 95 | .320 55 | .299 60 | .290 85 | .273 20 | .265 15 |
| e | .358 90 | .339 15 | .308 00 | .350 75 | .334 00 | .356 25 | .342 50 | .322 85 |

It is not the authors' contention, however, that physical significance is necessarily to be attached to the system of planes as derived, nor that the individual deviations represent merely experimental or random errors. On the contrary, if, by an examination of the magnitude and distribution of plus and minus departures from the calculated surface (recorded in fig. 5), the reader is enabled to form some conception of what the "true" surface would be, making due allowance for experimental error, then the solution here presented has fulfilled its chief purpose. If the latter viewpoint is taken, then the fact that a different number of parameters or some other grouping of the

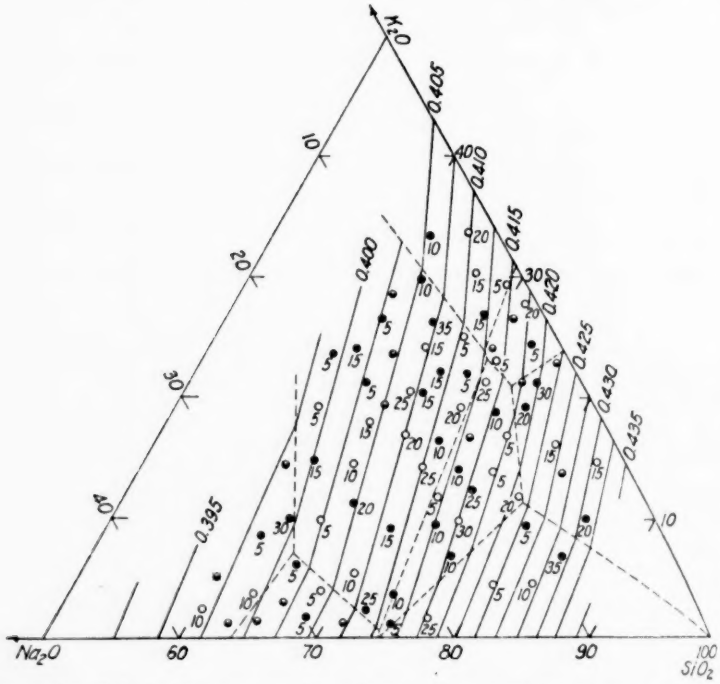



FIGURE 5.—*Relation between specific volume and composition of some soda-potash-silica glasses.*

Observed specific-volume values lie on (◒), above (●), or below (○), the computed surface, by the amounts indicated, times $10^{-3}$. Density deviations equal approximately six times these amounts.

points would lead to a different statistical solution becomes of minor importance, since the discrepancies between two such solutions would be compensated for by a correspondingly different pattern of departures. That is, the "true" surface conceivably would be indicated in either case. To the authors, the calculated surface here presented is a very good approximation to the "true" surface in view of the comparative absence of systematic deviation.

## V. DISCUSSION

If the specific volume-composition relations are compared to the liquidus curves of the appropriate equilibrium diagrams presented by Kracek [4, 5, 6, 7], one finds a surprising, if not significant, correspond-

ence. In the case of the soda-silica data (*B*, fig. 3), the two deflections occur at or near the eutectic compositions (See *B'*, fig. 3, at 63 and 75 percent $SiO_2$). In the potash-silica data (*A*, fig. 3), the deflection at 69 percent $SiO_2$ adequately reflects the eutectic at this composition (see *A'*, fig. 3). The other deflection occurs at about 76 percent $SiO_2$, and appears to correspond, not to the "true" eutectic (which is at about 72 percent $SiO_2$), but to the minimum point along the metastable cristobalite liquidus curve, which point is found under conditions more nearly comparable to the glassy state than those under which the "true" eutectic composition is found.

Concerning the soda-potash-silica data, the deflections (represented as lines of demarcation, fig. 4) correspond roughly to the boundary curves of the equilibrium diagram (dotted lines, fig. 4) connecting the eutectic compositions (small triangles, fig. 4) or other invariant points.

The plot of the specific volume-composition data thus far obtained on the lithia-silica glasses (*C*, fig. 2) is included here only for comparative purposes, since this phase of the work is far from complete. The two deflections—at about 78 and 82 percent $SiO_2$—are, however, the most pronounced observed for any series of glasses studied at this Bureau. The deflection at 82 percent $SiO_2$ corresponds to the eutectic at that composition, but the equilibrium diagram does not indicate a "critical composition" at 78 percent $SiO_2$.

A series of 10 boric oxide-silica glasses was reported by Cousens and Turner [8]. They plotted density as a function of composition and concluded that these data should be represented by a "smooth curve" showing no deflections—an apparent contradiction to the interpretation just given concerning our own data. It appears, however [9], that the eutectic, if any, in the boric oxide-silica system would occur very near to 100 percent $B_2O_3$, so that the existence of a corresponding deflection in the density-composition line could not easily be demonstrated, even if one were expected. Of interest, furthermore, is the fact that, when the specific volumes instead of the densities of their glasses are plotted against the compositions, the points are found to lie upon a single *straight* line connecting the specific volume of vitreous silica (0.4540) with that of vitreous $B_2O_3$, using for the latter the value 0.5440 as computed from the density reported by the same laboratory in a subsequent paper [10].[6]

## VI. SUMMARY

The foregoing presentation may be briefly summarized as follows:

1. Data are presented on the density and composition of 194 glasses in the ternary system soda-potash-silica.

2. A reproducible and, it is felt, consistent method of heat treatment is described which, when applied simultaneously to all the glasses, results in the cooling of each glass at the same rate through its own "critical range" as defined.

3. A study of the data presented does not indicate that there is a simple relationship between specific volume and composition, but that the relation is best expressed by a system of planes in a three-dimensional triordinate diagram whose intersections correspond fairly well to the boundary curves and eutectic compositions indicated by

[6] In that paper, the value reported in the earlier paper [8] was said to have been erroneous.

the equilibrium diagram of Kracek. The correspondence is very close for the soda-silica and potash-silica data, but it is only approximate for glasses containing all three constituents.

4. Data on the specific volume of 10 lithia-silica glasses are presented graphically.

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# VOLATILIZATION OF METALLIC COMPOUNDS FROM SOLUTIONS IN PERCHLORIC OR SULFURIC ACID

By James I. Hoffman and G. E. F. Lundell

ABSTRACT

Distillation from perchloric or sulfuric acid solutions, during the gradual addition of hydrochloric or hydrobromic acid to the hot solution (200° to 220° C), was undertaken to obtain information on the volatility under these conditions of elements that might be encountered in chemical analysis. It was found that, if proper conditions are established, antimony, arsenic, chromium, germanium, osmium, rhenium, ruthenium, and tin can be quantitatively distilled from perchloric acid, and germanium, arsenic, selenium, tin, antimony, and rhenium from sulfuric acid solutions. Certain others, as bismuth, boron, gold, molybdenum, tellurium, and thallium, may be lost in part from either perchloric or sulfuric acid solutions. From the information obtained, certain precautions against unintentional losses are evident, and certain possible separations of elements are indicated.

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## I. INTRODUCTION

Volatilization as chromyl chloride, $CrO_2Cl_2$, has been employed by Smith[1] as a means of eliminating chromium in determinations of manganese, nickel, and vanadium, in steels containing high percentages of chromium. Certain other chlorides, notably those of antimony, arsenic, germanium, mercury, selenium, and tin, are likewise known to be volatile at or below 200° C, the temperature at which chromyl chloride is distilled. The present work was undertaken to obtain further information on the elements mentioned, as well as on other elements that might be encountered in chemical analysis. In this, two distinct purposes were kept in mind. The first was to find possible separations of elements that can not be separated by distilling at temperatures below 200° C. The second was to obtain information on elements that might be lost unintentionally when solutions are evaporated with perchloric or sulfuric acid in such operations as dehydration of silicic acid or expulsion of fluorides. Distillations with hydrobromic acid were included because they are sometimes used, and because certain bromides are even more volatile than the corresponding chlorides.

[1] Fred Wilson Smith, Ind. Eng. Chem., Anal. Ed. **10**, 360 (1938); and Chemists U. S. Steel Corporation, Sampling and Analysis of Carbon and Alloy Steels, p. 70, 77, 132, and 157, (Reinhold Publishing Co., New York, N. Y., 1938 ed.)

## II. EXPERIMENTAL WORK

In Smith's procedure the steel is dissolved in an Erlenmeyer flask in a mixture of hydrochloric and perchloric acids, and the chromium is oxidized to the sexivalent state by heating the solution until copious fumes of perchloric acid are evolved. The chromium is then volatilized as chromyl chloride by adding successive small portions of sodium chloride or hydrochloric acid to the hot solution. At least 99 percent of the chromium is easily eliminated in this way.

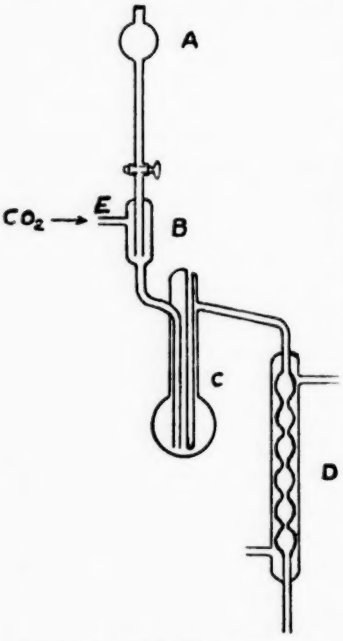


FIGURE 1.—*Distilling apparatus.*

In the present work, an Erlenmeyer flask was not suitable because it was desired to test the volatile portion as well as the residual solution in the flask. The distilling apparatus devised by J. A. Scherrer [2] is well suited for this purpose and has the added advantages that the hydrochloric or hydrobromic acid can be admitted at any desired rate, that the temperature of the solution can be observed at all times, and that rubber stoppers, which might cause serious explosions, are avoided.[3] The apparatus is illustrated in figure 1. The flask has a capacity of 200 ml, and the distance between the bottom of the flask and the outlet tube leading to the condenser is about 15 cm.

The following six types of distillations were investigated: (1) Distillation with perchloric and hydrochloric acids; (2) distillation with perchloric and hydrobromic acids; (3) distillation with perchloric, phosphoric, and hydrochloric acids; (4) distillation with perchloric, phosphoric, and hydrobromic acids; (5) distillation with sulfuric and hydrochloric acids; and (6) distillation with sulfuric and hydrobromic acids.

(1) *Procedure for distillation with perchloric and hydrochloric acids.*—To facilitate rapid heating of the contents of the flask, and at the same time to protect the upper portion of the flask from excessive heating, the bottom of the distilling flask was placed over a 4-cm hole in a wire gauze with asbestos center. The distillate was collected in a beaker containing 100 ml of cold distilled water, so placed that the tip of the condenser *D* was slightly immersed. From 25 to 100 mg of the element under test, usually in the form of a solution of its chloride or perchlorate, was introduced into the distilling flask through *A*; then

[2] J. Research NBS **16**, 255 (1936) RP871; **21**, 95 (1938) RP1116.

[3] *It should be remembered that at the temperatures used in this work perchloric acid is a powerful oxidizing agent and may therefore react with explosive violence if it comes in contact with certain reducing substances, such as organic matter.*

TABLE 1.—*Results obtained in distillations at 200 to 220° C*

| Element [1] | Approximate percentage volatilized from 20 to 100-mg portions by distillation with— | | | | | |
|---|---|---|---|---|---|---|
| | $HCl-HClO_4$ (Procedure 1) | $HBr-HClO_4$ (Procedure 2) | $HCl-H_3PO_4-HClO_4$ (Procedure 3) | $HBr-H_3PO_4-HClO_4$ (Procedure 4) | $HCl-H_2SO_4$ (Procedure 5) | $HBr-H_2SO_4$ (Procedure 6) |
| Ag | 0 | 0 | 0 | 0 | 0 | 0 |
| Alkali metals [2] | 0 | 0 | 0 | 0 | 0 | 0 |
| Al | 0 | 0 | 0 | 0 | 0 | 0 |
| $As^{III}$ | 30 | 100 | 30 | 100 | 100 | 100 |
| $As^{V}$ | 5 | 100 | 5 | 100 | 5 | 100 |
| Au | 1 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| B | 20 | 20 | 10 | 10 | 50 | 10 |
| Ba | 0 | 0 | 0 | 0 | 0 | 0 |
| Be | 0 | 0 | 0 | 0 | 0 | 0 |
| Bi | 0.1 | 1 | 0 | 1 | 0 | 1 |
| Ca | 0 | 0 | 0 | 0 | 0 | 0 |
| Cb | 0 | 0 | 0 | 0 | 0 | 0 |
| Cd | 0 | 0 | 0 | 0 | 0 | 0 |
| Co | 0 | 0 | 0 | 0 | 0 | 0 |
| $Cr^{III}$ | 99.7 | 40 | 99.8 | 40 | 0 | 0 |
| Cu | 0 | 0 | 0 | 0 | 0 | 0 |
| Fe | 0 | 0 | 0 | 0 | 0 | 0 |
| Ga | 0 | 0 | 0 | 0 | 0 | 0 |
| Ge [3] | 50 | 70 | 10 | 90 | 90 | 95 |
| Hf [4] | 0 | 0 | 0 | 0 | 0 | 0 |
| $Hg^{I}$ | 75 | 75 | 75 | 75 | 75 | 90 |
| $Hg^{II}$ | 75 | 75 | 75 | 75 | 75 | 90 |
| In | 0 | 0 | 0 | 0 | 0 | 0 |
| Ir | 0 | 0 | 0 | 0 | 0 | 0 |
| Mg | 0 | 0 | 0 | 0 | 0 | 0 |
| Mn | 0.1 | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 |
| Mo | 3 | 12 | 0 | 0 | 5 | 4 |
| Ni | 0 | 0 | 0 | 0 | 0 | 0 |
| Os [5] | 100 | 100 | 100 | 100 | 0 | 0 |
| P | 1 | 1 | 1 | 1 | 1 | 1 |
| Pb | 0 | 0 | 0 | 0 | 0 | 0 |
| Pd | 0 | 0 | 0 | 0 | 0 | 0 |
| Pt | 0 | 0 | 0 | 0 | 0 | 0 |
| Re | 100 | 100 | 80 | 100 | 90 | 100 |
| Rare earths [6] | 0 | 0 | 0 | 0 | 0 | 0 |
| Rh | 0 | 0 | 0 | 0 | 0 | 0 |
| Ru | 99.5 | 100 | 100 | 100 | 0 | 0 |
| $Sb^{III}$ | 2 | 99.8 | 2 | 99.8 | 33 | 99.8 |
| $Sb^{V}$ | 2 | 99.8 | 0 | 99.8 | 2 | 98 |
| $Sb^{IV}$ | 4 | 2 to 5 | 2 to 5 | 2 to 5 | 30 | 100 |
| $Se^{VI}$ | 4 | 5 | 5 | 5 | 20 | 100 |
| Si | 0 | 0 | 0 | 0 | 0 | 0 |
| $Sn^{II}$ | 99.8 | 100 | 0 | 99.8 | 1 | 100 |
| $Sn^{IV}$ | 100 | 100 | 0 | 100 | 30 | 100 |
| Sr | 0 | 0 | 0 | 0 | 0 | 0 |
| Ta | 0 | 0 | 0 | 0 | 0 | 0 |
| $Te^{IV}$ | 0.5 | 0.5 | 0.1 | 0.5 | 0.1 | 10 |
| $Te^{VI}$ | 0.1 | 0.5 | 0.1 | 1 | 0.1 | 10 |
| Th | 0 | 0 | 0 | 0 | 0 | 0 |
| Ti | 0 | 0 | 0 | 0 | 0 | 0 |
| $Tl^{I}$ | 1 | 1 | 1 | 1 | 0.1 | 1 |
| U | 0 | 0 | 0 | 0 | 0 | 0 |
| V | 0.5 | 2 | 0 | 0 | 0 | 0 |
| W | 0 | 0 | 0 | 0 | 0 | 0 |
| Zn | 0 | 0 | 0 | 0 | 0 | 0 |
| Zr | 0 | 0 | 0 | 0 | 0 | 0 |

[1] Valences given in this column are those of the elements in the distilling flask at the beginning of the distillation.

[2] This includes lithium, sodium, potassium, rubidium, and cesium.

[3] The results given here are those obtained by heating the sulfuric or perchloric acid solutions in the distilling flask to 200° C before admitting the hydrochloric or hydrobromic acid. During the heating, $GeO_2$ separated. By adding hydrochloric or hydrobromic acid to the solution before heating, separation of $GeO_2$ did not occur, and the germanium readily passed into the distillate.

[4] Since pure hafnium was not available, this test was made by decomposing 2 g of cyrtolite and distilling as indicated. Spectrochemical tests showed that hafnium was one of the constituents of the mineral. It is supposed to contain 3 to 5 percent of $HfO_2$.

[5] At 200 to 220° C no osmium was volatilized from the solutions containing sulfuric acid; however, at 270 to 300° C the osmium was completely volatilized.

[6] This includes scandium, yttrium, and lanthanum in addition to the rare earths, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutecium. A mixture in which all these elements were known to be present was used in this distillation.

[7] In distilling from sulfuric acid, a few tests were made in which hydrochloric acid containing sulfurous acid was added to the hot sulfuric acid solution in the distilling flask. This was done to keep the thallium in the univalent state. No thallium was found in the distillates, whereas a little (about 1 mg) was always found if the thallium was first oxidized.

15 ml of 60-percent perchloric acid was added, and the stopcock was closed. A moderate stream of dry carbon dioxide was admitted through tube *E* and bubbled through the solution in the distilling flask. This swept the vapors from the flask into the condenser and prevented bumping by keeping the solution agitated. After the stream of gas was started, the contents of the flask were rapidly heated to 200° C with a Tirrill burner. The temperature was observed with a thermometer placed in the thermometer well of the flask. Hydrochloric acid, sp gr 1.18, from bulb *A* was now introduced through the inlet tube beneath the surface of the hot solution in the flask at such a rate that the temperature remained between 200° and 220° C. After 15 ml of hydrochloric acid had been admitted, during the course of 20 to 30 minutes, the distillation was stopped, and the distillate and residual solution in the flask were examined.

(2) *Distillation with perchloric and hydrobromic acids.*—The same procedure was used as in (1), except hydrobromic acid (the 40-percent reagent) was substituted for hydrochloric acid.

(3) *Distillation with perchloric, phosphoric, and hydrochloric acids.*—The same procedure was used as in (1), except 5 ml of sirupy phosphoric acid was added to the contents of the flask before the solution was heated and the hydrochloric acid admitted.

(4) *Distillation with perchloric, phosphoric, and hydrobromic acids.*—The same procedure was used as in (3), except hydrobromic acid was substituted for hydrochloric acid.

(5) *Distillation with sulfuric and hydrochloric acids.*—This corresponded exactly with (1), except sulfuric acid (sp gr 1.84) was substituted for perchloric acid.

(6) *Distillation with sulfuric and hydrobromic acids.*—This corresponded with (2), except sulfuric acid was substituted for perchloric acid.

The results of the tests are given in table 1.

## III. DISCUSSION OF RESULTS

### 1. SEPARATION OF CHROMIUM

This work confirms the statement of Smith [4] that by distilling with perchloric and hydrochloric acids chromium can be satisfactorily separated from manganese in analyses of steels containing high percentages of chromium. The amount of manganese volatilized is entirely negligible in any ordinary analysis.[5]

### 2. SEPARATIONS OF OTHER ELEMENTS

Complete distillation can probably be obtained in a reasonable time with those elements in table 1 that have passed into the distillate to the extent of 50 percent or more, but such a procedure would most likely be impractical in the case of boron.

The table shows that arsenic, antimony, and tin can be volatilized, and additional work indicates that a practical method can probably be

[4] Ind. Eng. Chem., Anal. Ed. **10**, 360 (1938).

[5] For example, in determinations of manganese in 1-g samples of 18 chromium-8 nickel steel (NBS Standard Sample 101) after volatilizing the chromium as chromyl chloride, 0.559 and 0.553 percent, respectively, were obtained as compared with the certificate value, 0.555 percent.

developed for separating small percentages of these from as much as 5 g of lead, by distilling with hydrobromic and perchloric acids at 200° to 220° C.

If the reactions of the neighboring elements in the periodic system can be used as a criterion, it should be possible to volatilize the element masurium by distilling with perchloric and hydrochloric acids.

Selenium can be separated from many other elements by distillation with hydrobromic and sulfuric acids [6] (procedure 6).

Rhenium can be separated from molybdenum by distilling from a mixture of perchloric and phosphoric acids to which hydrobromic acid is slowly added (procedure 4). In a distillation involving 0.25 g of molybdenum, the presence of molybdenum was detected in the distillate, but the amount was less than 0.05 mg.[7]

Since preliminary experiments indicated that molybdenum can be volatilized in part by distilling at 200° to 220° C with sulfuric and hydrochloric acids or with sulfuric and hydrobromic acids, additional distillations were made at temperatures as high as 300° C in an attempt to get complete separation of molybdenum. These distillations were continued for at least one hour, and as much as 50 ml of the halogen acids was used. Even with these more drastic treatments, volatilization was far from complete. The use of dry gaseous hydrogen chloride with either perchloric or sulfuric acid likewise failed to effect sufficient volatilization to offer promise of a separation of molybdenum from such elements as tungsten or iron.

### 3. LOSSES THAT MAY CAUSE ERRORS IN ANALYTICAL PROCEDURES

An inspection of table 1 is sufficient to show that many elements may be lost entirely or in part in evaporations with sulfuric or perchloric acid in many of the usual analytical operations. The losses indicated for gold, bismuth, molybdenum, phosphorus, tellurium, vanadium, and thallium are small, but may cause serious error if the material being analyzed contains high percentages, as for example, gold in dental gold alloys. On the other hand, with the usual small amounts of vanadium in steels, the loss in distillations with perchloric and hydrochloric acids is seldom of any consequence.

Loss of chromium during its oxidation with perchloric acid likewise is of importance. If hydrochloric acid is present during the oxidation, chromyl chloride may be formed and volatilized. A slight loss of chromium may occur even if no hydrochloric acid is added before or during the oxidation with perchloric acid, because hydrochloric acid is probably one of the products of the reaction when trivalent chromium is oxidized by perchloric acid. In five experiments in which 0.1 g of chromium as the sulfate was oxidized with perchloric acid and heated for 5 minutes at 200° to 220° C in the apparatus illustrated in figure 1, from 0.2 to 0.4 mg of chromium was found in the distillates. This probably is the chief cause for the slightly low results

[6] See also A. A. Noyes and W. C. Bray, A System of Qualitative Analysis for the Rare Elements, p. 37 and 292 (The Macmillan Co., New York, N. Y., 1927).

[7] For the distillation of rhenium from phosphoric acid solution, see W. Geilman und F. Weibke, Z. anorg. allgem. Chem. **199**, 126 (1931).

obtained in the determination of chromium by oxidation with perchloric acid.[8] Of interest is the action of phosphoric acid in preventing volatilization of vanadium, molybdenum, tin, and bismuth in the hydrochloric-phosphoric-perchloric acid series (procedure 3), or of vanadium and molybdenum in the hydrobromic-phosphoric-perchloric acid series (procedure 4).

WASHINGTON, February 17, 1939.

[8] G. E. F. Lundell, J. I. Hoffman, and H. A. Bright, Chemical Analysis of Iron and Steel, p. 208 (J. Wiley & Sons, New York, N. Y., 1931 ed.), and Chemists U. S. Steel Corporation, Sampling and Analysis of Carbon and Alloy Steels, p. 70 (Reinhold Publishing Co., New York, N. Y., 1938 ed.).

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# DETERMINATION OF PENTOSANS IN PULPS AND PAPERS

By Herbert F. Launer and William K. Wilson

ABSTRACT

A relatively rapid method for the determination of pentosans in pulps and papers is described. A simple volumetric procedure was adapted to the analysis of the distillates for furfural. With minor changes, the simple method of distillation prescribed by the Association of Official Agricultural Chemists was retained, since a comparison, using a variety of pulps, showed that various other methods gave no higher yields of furfural. For example, distillation in a current of steam from hydrochloric acid nearly saturated with ammonium chloride greatly increased the yield of volatile material, perhaps hydroxymethylfurfural, from cellulose, but not of furfural from pentosans. The error due to volatile material other than furfural in the AOAC distillates was found to be 0.9 percent, in terms of pentosan, for all of the usual wood pulps. This correction was determined by two independent methods, namely, fractionation of the distillates by redistillation, and study of the rates of evolution of volatile material. Experiments also showed that the volatile material from a typical cotton fiber arose mainly from substances other than pentosans.

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## I. INTRODUCTION

The method generally used [1] for the estimation of pentosans specifies distillation of the material with 12-percent hydrochloric acid until 360 ml is collected in 120 minutes. The furfural in the distillate is then precipitated and weighed as the phloroglucide, from which the weight of the pentosan is calculated, using Kröber's tables. Ordinary distilling apparatus, with water-cooled condenser, is used. A separatory funnel mounted above the distilling flask contains the acid which is added in portions during the distillation. This arrangement, with the simple modification of attaching the receiver to the end of the condenser by means of an adapter and rubber stoppers, will be referred to subsequently as the "simple" distilling apparatus.

Both the distillation and the furfural determination have been the subject of much study. Pervier and Gortner,[2] among others, have

[1] Official and Tentative Methods of the Association of Official Agricultural Chemists, p. 344 (1935). See also *Methods used at the Forest Products Laboratory*, Paper Trade J. 87, 67 (December 20, 1928).

[2] N. C. Pervier and R. A. Gortner, Ind. Eng. Chem. 15, 1169, 1255 (1923). This contains a bibliography and a rather comprehensive discussion of the subject.

suggested that furfural may be partially decomposed by the hot hydrochloric acid under the conditions of the distillation, and therefore, that the furfural should be removed as quickly as possible by a current of steam. Kullgren and Tyden [3] found a 3-percent loss in attempting to recover known quantities of furfural by distilling from hydrochloric acid saturated with sodium chloride to salt out the furfural. Kline and Acree [4] found no essential difference between the results of steam and simple distillation. Recently, Hughes and Acree [5] reported quantitative conversion of xylose to furfural by distilling in a current of steam from hydrochloric acid saturated with sodium chloride.

Much of the work on the development of a method for determining pentosans has been rendered difficult of interpretation owing to the lack of a sufficiently simple and accurate method for estimating furfural. The use of phloroglucinol and other precipitants has many disadvantages other than those usually associated with gravimetric methods.[3 4] Of the volumetric methods proposed, that used by Powell and Whittaker,[6] with the modification by Hughes and Acree,[7] appears to be the simplest and most accurate. In this method a known excess of potassium bromate-bromide is added to the cold (0 to 2° C) furfural-hydrochloric acid solution in a special side-arm flask and the liberated bromine allowed to react for 5 minutes, after which the unused bromine is determined iodometrically. With this method the last-named authors were able to determine furfural within 0.35 percent, on an average, of the known amount.

Various workers, especially Kullgren and Tyden, have shown that volatile compounds other than furfural, for example, hydroxymethylfurfural from hexoses, may be present in distillates from wood pulps. Cunningham and Doree [8] report that the amounts of furfural and hydroxymethylfurfural obtainable from cotton may be varied by previous chemical treatments, their results being based upon the difference in solubilities of the phloroglucides.

The present work was undertaken to adapt, if possible, the results of recent developments in the furfural determination and in the distillation procedure to a simple and relatively accurate method for the determination of pentosans in pulps and papers. Steam distillation with ammonium chloride, which is much more soluble than sodium chloride in hot hydrochloric acid, and therefore may be more effective for salting out the volatile products, was investigated for possible increased yields of furfural from pentosans. An effort, furthermore, was made to determine the amount of volatile material arising from cellulose during the pentosan distillation, and to arrive at a value for the correction which would be generally applicable in determinations of pentosans in pulps and papers.

[3] C. Kullgren and H. Tyden, Ing. Vetenskaps Akad., Handl. **94**, 3-62 (1929).
[4] G. M. Kline and S. F. Acree, BS J. Research **8**, 25 (1932) RP398.
[5] Elizabeth E. Hughes and S. F. Acree, J. Research NBS **21**, 329 (1938) RP1132.
[6] W. J. Powell and H. J. Whittaker, J. Soc. Chem. Ind. **43**, 35T (1924).
[7] Elizabeth E. Hughes and S. F. Acree, Ind. Eng. Chem., Anal. Ed. **6**, 123 (1934).
[8] M. Cunningham and C. Doree, Biochem. J. **8**, 445 (1914).

## II. EXPERIMENTAL RESULTS AND DISCUSSION

### 1. DETERMINATION OF FURFURAL

Known quantities of a standard aqueous solution of furfural [9] were added to a solution of hydrochloric acid in 1-liter glass-stoppered reagent bottles, to make 350 ml of a solution, 2.7 *N* in HCl.[10] Two hundred and fifty g of crushed ice was added and after the temperature had fallen to −2° to 0° C, 20.00 ml of a 0.2 *N* solution of potassium bromate, containing 50 g of potassium bromide per liter, was added. The bottles were then closed and the contents thoroughly mixed. After 5 minutes, 10 ml of a 10-percent solution of potassium iodide was added. After the remaining bromine had been completely absorbed, the liberated iodine was titrated with thiosulfate using starch indicator. Representative results are given in table 1, series 1 to 4. Series 5 is presented to show that essentially the same value for the amount of furfural in 20.00 ml of standard solution was obtained, using either ordinary reagent bottles or special sidearm flasks [11] in the determination.

TABLE 1.—*Determination of furfural*

| Series | Bromine used: in terms of 0.09931 *N* thiosulfate solution | Furfural found | Deviations from known value |
|---|---|---|---|
| | *Milliliters* | *Grams* | *Percent* |
| 1. 25 ml of furfural solution = 0.1250 g | 26.24 | 0.1251 | 0.1 |
| | 26.27 | .1252 | .2 |
| | 26.29 | .1253 | .2 |
| Average | | 0.1252 | 0.2 |
| 2. 20 ml of furfural solution = 0.09997 g | 21.00 | 0.1001 | 0.1 |
| | 21.01 | .1001 | .1 |
| | 21.01 | .1001 | .1 |
| Average | | 0.1001 | 0.1 |
| 3. 10 ml of furfural solution = 0.04998 g | 10.47 | 0.04991 | −0.1 |
| | 10.47 | .04991 | −.1 |
| | 10.53 | .05019 | .4 |
| Average | | 0.05000 | 0.1 |
| 4. 5 ml of furfural solution = 0.02499 g | 5.23 | 0.02493 | −0.2 |
| | 5.25 | .02503 | .1 |
| | 5.23 | .02493 | −.2 |
| Average | | 0.02496 | −0.1 |
| 5. 20 ml of furfural solution = 0.0997 g. (Special flask used.) | 20.92 | 0.09972 | −0.2 |
| | 21.01 | .1001 | .1 |
| | 20.94 | .09982 | −.2 |
| Average | | 0.09988 | −0.1 |

[9] The furfural was distilled under reduced pressure, 190 mm, at 118° C, to obtain an almost water-white product. From the middle one-third fraction 9.997 g was then weighed out for 2 liters of solution. The amount of furfural lost by volatilization during the weighing was found to be 0.3 mg.

[10] The usual concentration of acid in the pentosan distillates in the procedure to be described is 2.7 *N* after dilution. Further dilution by the melting ice and by the reagents added usually reduces the acidity to 1.3 *N* when the solutions are ready for titration with thiosulfate.

[11] Elizabeth E. Hughes and S. F. Acree, Ind. Eng. Chem., Anal. Ed. **6**, 292 (1934). These flasks have two sidearms to contain the bromate and iodide so that these reagents may be added without opening the flasks at the risk of losing bromine. Very little bromine is lost when the 1-liter glass-stoppered reagent bottles are used, however, provided that the stopper is replaced without delay after addition of the iodide. Experiments in which 20.00 ml of bromate-bromide solution was titrated under test conditions in both the sidearm flasks and the reagent bottles showed the average volumes 40.72 and 40.66 ml, respectively, of 0.1 *N* thiosulfate solution necessary. This loss, corresponding to 0.15 percent of bromine, results in an error which is smaller than the average deviation in table 1, provided that the blank is determined under test conditions.

The use of crushed ice makes it possible to cool very quickly to 0° to −2° C. This temperature interval appears especially favorable for limiting the reaction between furfural and bromine to a molar ratio of 1:1. The quantities of reagents used make the method applicable to the analysis of the ordinary pulps and papers without the necessity of taking aliquot portions.

It is to be noted that the precision shown in table 1 is actually much higher than is required for a pentosan method, inasmuch as an error of 0.1 percent in the amount of furfural corresponds to an error of 0.01 percent in the pentosan content of a material containing 10 percent of pentosans.

## 2. COMPARISON OF METHODS OF DISTILLATION, USING PULPS AND PAPERS CONTAINING PENTOSANS

In order to compare the results obtained by simple distillation with those obtained by distilling in a current of steam from hydrochloric acid saturated with sodium chloride, the latter to be referred to subsequently as "distillation with NaCl+steam," the simple distilling apparatus was used with certain changes. The 1-liter reagent bottles serving as receivers were connected by means of an adapter and rubber stoppers to the end of the condenser, thus forming a closed system, except for a small U-trap [12] containing 5 ml of water and glass beads, which was mounted in the rubber stopper of the receiver. In addition to this, for the distillations with steam, a glass tube drawn out to a small diameter projected 1 cm below the surface of the liquid in the distilling flask, and admitted the steam from a large flask of boiling distilled water. Twenty grams of sodium chloride was added to the distilling flask.

In the simple distillation, 1 g of pulp or paper was added to 100 ml of 12-percent (3.5 *N*) hydrochloric acid in the distilling flask. During continual dropwise addition of more acid, 300 ml was distilled in 90 to 100 minutes. It will be shown later that this is satisfactory for most cases; for the time being relative values only are required. Fifty ml of water was then added to the distillate, and the furfural determination was carried out in the manner just described. When steam was used, the volume of condensate was 625±40 ml. Since acid had been added in the same amount and manner as before, the acidities of the condensates varied, which necessitated titration of a portion with standard alkali. Weight-aliquots were then taken and sufficient concentrated hydrochloric acid added to give 350 ml, 2.7 *N* in HCl, after which the furfural determination was made as before.

The results of the distillations are listed in table 2 and show that the use of NaCl+steam produces higher "pentosan" values than the simple distillation in each case. On the basis of these results it seemed desirable to use a salt which is more soluble in the hot hydrochloric acid than sodium chloride. Accordingly, experiments were carried out in which 55 g of $NH_4Cl$ instead of 20 g of NaCl was used, but which were the same in all other respects. The results are given in table 2

[12] Such a trap was recommended by Hughes and Acree, but was found to be superfluous in these pentosan distillations. In 12 distillations of material containing 11 to 19 percent of pentosans, corresponding to 0.1 to 0.17 g of furfural, never more than 0.1 mg and usually 0.1 mg of furfural was found in the trap. Since this corresponds to some 0.01 to 0.02 percent of pentosans, and is of the same order of magnitude as the experimental error, such corrections may be neglected. If the condensate in the receiver is warm, either because of too rapid distillation or inefficient cooling in the condenser, it is possible that the higher vapor pressure of furfural in the receiver may cause low results if a trap is not used. The temperature of all condensates in the present work was approximately 25° C.

and show that "pentosan" values in the distillations with $NH_4Cl$+steam are higher in every case than in the simple distillations or in those with NaCl+steam. Blank runs with the salts, but without the cellulose materials, showed negligible amounts of oxidizable substances, less than 0.05 percent expressed as pentosan, in the distillates.

TABLE 2.—*Comparison of the "pentosan" values obtained by using various methods of distillation*

| Samples [a] | Type of distillation | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Simple distillation | | Sodium chloride with steam | | | Ammonium chloride with steam | | |
| | "Pentosan" values | | "Pentosan" values | | Gain over simple (% pentosan) | "Pentosan" values | | Gain over simple (% pentosan) |
| | *Percent* | *Average* | *Percent* | *Average* | | *Percent* | *Average* | |
| *C*, new rag paper | 0.7, .8, .7, .7 | 0.7 | 1.0, 1.2, 1.2 | 1.1 | 0.4 | 2.1, 1.8, 2.1 | 2.0 | 1.3 |
| *E*, special sulfite pulp | 2.9, 2.8, 2.9, 3.0 | 2.9 | 3.2, 3.2, 3.1 | 3.2 | 0.3 | 4.2, 4.6, 3.7, 4.2, 4.9 | 4.3 | 1.4 |
| *F*, sulfite pulp | 4.7, 4.8, 4.8 | 4.8 | | | | 6.1, 6.4, 6.3, 5.8 | 6.2 | 1.4 |
| *I*, soda-sulfite (1:1) paper | 11.2, 11.0, 11.0, 11.0, 10.9 | 11.0 | 11.6, 11.3 | 11.4 | 0.4 | 12.8, 12.6 | 12.7 | 1.7 |
| *H*, soda pulp | 16.3, 16.1, 16.1 | 16.2 | 16.9, 16.3, 16.8, 16.4 | 16.6 | 0.4 | 18.8, 18.7, 19.1, 19.0, 18.1, 17.8 | 18.6 | 2.4 |

[a] The fiber contents of these samples, after correction for moisture, ash, and resin were, in the order listed, 0.92, 0.92, 0.91, 0.91, and 0.92 g, respectively.

The gains shown in column 6 are not of the magnitude to be expected if the distillations with NaCl+steam are instrumental in increasing the conversion of pentosans to furfural. Considering for the moment only the wood fibers, *E*, *I*, and *H*, the gain for sample *E* is 10 percent, whereas the gains for samples *I* and *H* are 3.6 and 2.5 percent, respectively. On the other hand, the gains correspond closely to those which would be expected if the distillation with NaCl+steam had the effect of increasing the yield of such unstable compounds as hydroxymethylfurfural, the amount of which is a function of the cellulose rather than of the pentosan content. This is further brought out by the results with the rag (cotton) sample *C*, where the percentage gain as a pentosan product would be very high, but as a cellulose product would be in good agreement with the other results.

These points are emphasized by the results obtained by using $NH_4Cl$+steam. The gains in volatile material, especially for samples *C*, *E*, and *F*, are obviously more related to the cellulose content (see footnote [a] of table 2) than to the "pentosan" content, which latter varied some sevenfold.

There is, however, another method of deciding upon the cause of the gain in volatile material shown in table 2. Kullgren and Tyden have shown that volatile material from glucose is completely destroyed upon redistillation, under conditions essentially those of the simple distillation, but with sodium chloride in the distilling flask. Furthermore, upon redistilling the distillate from a sulfite pulp, they found that volatile material corresponding to 1.1 percent of pentosan was destroyed, after applying a correction for losses of furfural. Since furfural can be distilled with small, fairly constant losses, as Kullgren and Tyden have found, any greater losses upon redistillation of the distillates must be ascribed to the decomposition of volatile material other than furfural.

The "simple" and the "$NH_4Cl$+steam" distillates from the two most common pulps, sulfite and soda, were subjected to repeated redistillation without steam or added salt. The distillates were weighed after each redistillation, and a weight-aliquot was taken for analysis. A small aliquot was also titrated with standard alkali for the purpose of determining how much hydrochloric acid and water were necessary to give the required acidity for analysis. The remainder was redistilled each time by adding 100 ml of it to the distilling flask, and allowing the rest to replace the distilling liquid by dropwise addition from the funnel. After the funnel was emptied in this manner, 110 ml of 12-percent hydrochloric acid was added dropwise and distillation continued until this also had been distilled. Thus, the volume of liquid in the distilling flask was always 100 ml. The final 110 ml of acid was shown by the work of Kullgren and Tyden to be necessary to complete the distillation of furfural.

The results of such repeated redistillations are given in table 3. The corrected values were calculated from the uncorrected values by taking into account the small losses of furfural itself during a distillation. This method of calculation, and the magnitude of the losses of furfural for the type of apparatus used, will be dealt with in the next section. The results, both corrected and uncorrected, show that large amounts of volatile material far less stable than furfural are contained in the original distillates from the pulps. This is especially true for the $NH_4Cl$+ steam distillates. The results also show that after one or more redistillations the unstable volatile material has been destroyed, and an essentially unchanging amount of stable volatile material, presumably furfural, remains, irrespective of initial "pentosan" values.

This confirms the previous conclusion that the higher "pentosan" values, obtained by distilling from salt solutions in a current of steam, are due to an increased yield of a volatile material other than furfural, probably hydroxymethylfurfural, from cellulose.

It does not appear advisable, therefore, to replace the much simpler distillation now in general use in the pentosan determination by either the NaCl or $NH_4Cl$+steam procedures. Furthermore, the use of such salts to salt out the volatile reaction products in this or similar distillations should be followed by some method of identifying the components of the distillates. Kullgren and Tyden distinguished

between the volatile products by redistilling once, and a proposed method for the determination of pentosans [13] has been based upon their procedure; but it is evident from table 3 that one such redistillation may not suffice for all cases.

TABLE 3.—*Effect of redistillation of "pentosan" distillates*

[Percentage of "pentosan." All redistillations by "simple" method]

| Type of original distillation | Original distillate from pulp | First redistillation of distillate | | Second redistillation of distillate | | Third redistillation of distillate | |
|---|---|---|---|---|---|---|---|
| | Uncorrected average * | Uncorrected | Corrected average | Uncorrected | Corrected average | Uncorrected | Corrected average |
| **Sulfite pulp, Sample *F*** | | | | | | | |
| Simple | 4.8 | 3.79<br>3.93 | 4.0 | 3.73<br>3.88 | 4.0 | 3.71<br>3.76 | 4.0 |
| Ammonium chloride with steam | 6.2 | 4.16<br>4.16<br>4.33<br>4.20 | 4.3 | 3.68<br>3.85<br>3.69<br>3.88 | 4.0 | (3.27)<br>3.73<br>3.55<br>3.58 | 3.9 |
| **Soda pulp, Sample *H*** | | | | | | | |
| Simple | 16.2 | 15.45<br>15.38 | 15.8 | 14.59<br>14.60 | 15.3 | 14.25<br>14.34 | 15.4 |
| Ammonium chloride with steam | 18.6 | 15.55<br>15.38<br>15.72 | 15.9 | 15.17<br>14.62<br>14.81 | 15.6 | 14.70<br>14.25<br>14.50 | 15.6 |
| **Cotton rag paper, Sample *C*** | | | | | | | |
| Simple | 0.7 | 0.37<br>.26<br>.30 | 0.3 | 0.14<br>.33<br>.26 | 0.2 | 0.23<br>.21<br>.20 | 0.2 |

* The average values in this column were taken from table 2.

The method used in this publication for calculating pentosan content is based upon the assumption of theoretical conversion of pentosans to furfural, and the expression is given in the last section. The methods of calculating pentosan content in use at the present time are based upon an assumed conversion of 80 percent, which is a purely arbitrary figure. It was never actually determined with pentosans, since no distillation with a pure pentosan has been reported but was taken as the approximate average of 88 and 74 percent, which are the observed percentage conversions to furfural of the respective pentoses, xylose and arabinose. Recently, Hughes and Acree reported 100-percent conversion of xylose to furfural, by use of the NaCl+ steam procedure. In the present work, it was found that neither this procedure nor one much more suitable for decreasing the decomposition of volatile material, $NH_4Cl$+steam, was found to increase significantly

[13] Charles Doree, The Methods of Cellulose Chemistry, p. 367 (Chapman and Hall, Ltd. London, 1933).

the yield of furfural from pentosans. It appears, therefore, to be a sounder practice to assume a theoretical conversion of pentosans to furfural for the basis of calculation, since minimum pentosan content is thereby attained. As a minimum value, a pentosan content may have a definite significance.

The reproducibility of the method involving simple distillation is satisfactory. In applying this method to the routine analysis [14] of 68 samples of pulps and papers at this Bureau, the average agreement between duplicates was 0.16 percent of pentosan. The duplicability of the methods employing steam distillation is affected by the variations in volume of steam passed. Such variations were difficult to control, which is reflected in the large variations in some of the results in table 2.

### 3. RECOVERY OF FURFURAL BY SIMPLE DISTILLATION

Known quantities of a standard solution of furfural were added to hydrochloric acid in the distilling flask, to make 100 ml of a solution, 12 percent by weight in hydrochloric acid. While continually adding more acid, 300 ml was distilled in 90 minutes in the simple distilling apparatus, after which 50 ml of water and 250 g of ice were added to the distillate, in which the furfural was then determined. The results given in table 4 show that the average loss in distilling amounts of furfural corresponding to the range of 4 to 19 percent of pentosan, is 3.1 percent of the furfural taken for distillation. This loss is somewhat lower than that found by Kullgren and Tyden, whose experiments, under similar conditions, showed a loss of 5 percent. They do not state, however, how the distillates were protected from air currents during the distillation, and the discrepancy can be explained by assuming that these workers used the usual method of allowing the distillate to drip from the condenser onto a paper filter held in a funnel. This is an ideal arrangement for causing volatilization of furfural, and was avoided in the present work.

TABLE 4.—*Loss of furfural during the simple distillation*

| Series | Furfural taken for distillation [a] | Furfural found in distillate | Loss of furfural | Loss of furfural |
|---|---|---|---|---|
| | *Grams* | *Grams* | *Grams* | *Percent* |
| 1 | 0.125 2 | 0.121 6 | 0.003 6 | 2.9 |
| | .125 2 | .121 5 | .003 7 | 3.0 |
| 2 | .100 1 | .098 29 | 001 8 | 1.8 |
| | .100 1 | .098 34 | .001 8 | 1.8 |
| 3 | .050 00 | .048 91 | .001 1 | 2.2 |
| | .050 00 | .048 60 | .001 4 | 2.8 |
| 4 | .024 96 | .023 74 | .001 2 | 4.8 |
| | .024 96 | .023 69 | .001 3 | 5.2 |
| Average | | | | 3.1 |

[a] The values in this column are the same as the average determined values in table 1, column 3.

As a matter of fact, however, high precision in the value of the correction is not necessary in the usual pentosan determination, because it has already been indicated that for a material containing 10 percent of pentosan any error in the amount of furfural is only one-tenth as large in terms of pentosan percentage.

[14] Performed by C. I. Pope.

The pentosan values in table 2 were not corrected for losses in furfural, since the values evidently represent more than pentosans alone. This does not detract from their usefulness, however, since only relative values were needed.

The corrected values in table 3 were obtained by dividing the average uncorrected value by $(0.976)^n$, where $n$ is the number of the redistillation, either 1, 2, or 3. The figure 0.976 corresponds to a recovery of 97.6 percent, or a loss of 2.4 percent, the average loss upon distilling quantities of furfural in the range 0.05 to 0.125 g of furfural. The average for this range, rather than the 3.1 average of table 4, was taken after it was observed that the use of the latter caused the values of table 3 to rise with succeeding distillations. This evidence, together with the fact that the percentage loss in the case of the smallest amount of furfural of table 4 is abnormally high, appears to warrant the omission of the latter from an average to be applied to redistillations from soda pulp, inasmuch as the amount of furfural involved therein, 0.10 g, is rather far removed from the smallest quantity of furfural listed in table 4. For the sulfite pulp, either average may be used without significant differences in individual values. To correct for furfural losses during a distillation from a pulp, however, the recovery may be taken as 0.97, since this is not raised to a higher exponential power, and leads to the approximate factor 1.03.

By applying this type of correction, the amount of furfural in the original distillate may be calculated from the subsequent redistillations. This is not strictly true for the first redistillation, since not all of the unstable volatile material had been destroyed at this point.

### 4. VOLATILE MATERIAL ARISING FROM CELLULOSE DURING THE SIMPLE DISTILLATION

The results in table 3 showed that volatile material from substances other than pentosans is included in the original "pentosan" distillates from common wood pulps, in the simple distillation procedure. By subtracting the values of the second or third redistillation from that of the original "simple" distillate, a difference of approximately 0.8 percent for both sulfite and soda pulps, calculated as a pentosan, is seen to represent the unstable volatile material which is not furfural. The value of 0.8 is a minimum, since the values for the last two redistillations may represent other stable volatile materials beside furfural. This value is in good agreement with that of 1.1 percent, obtained by Kullgren and Tyden using a sulfite pulp, inasmuch as these workers distilled from solutions of hydrochloric acid saturated with NaCl, which procedure yields greater quantities of unstable volatile material in the original distillate than the simple procedure used in the present work.

The value of 0.8 appears to be a correction which could be applied to the results of simple distillations of wood pulps, in order to arrive at a more nearly correct pentosan value. It would be desirable, however, to check this value by an independent method. This appears to be possible by studying the rate of the simple distillation beyond the first 300 ml, and then extending the rate data back through the first 300-ml period.

Accordingly, the distillation was subjected to further study. By continuing the addition of 12-percent hydrochloric acid and distillation beyond the first 300 ml on a group of materials derived from wood

and cotton, it was found that additional volatile material was obtained in all cases. In table 5 the roman numerals represent the distillate fractions. The calculations were carried out as though all volatile substances had arisen from pentosans. Under I are listed the initial values of the materials, obtained in the "simple" distillation of 300 ml in 90 to 100 min. The succeeding fractions were each 300 ml for the materials derived from cotton, and 150 ml for those derived from wood, distilled at the usual rate. The fractions were diluted to 350 ml with water and, whenever necessary, with hydrochloric acid before the addition of ice and bromate-bromide solution. Distillation of all samples beyond the first 300 ml was continued until the amount of volatile material per 150 ml of distillate became of the same order of magnitude as the experimental uncertainty.

The behavior of the wood pulps *D*, *E*, and *F*, beyond fraction I, and pulps *G* and *H* beyond fraction II, is in all cases so similar as to suggest that the volatile material in these fractions arose from the same source. The small differences between given fractions for the various materials are of the same order of magnitude as differences between given fractions of duplicate samples, not shown for the sake of clarity. Inasmuch as the amounts of cellulose present in the samples *D* to *H* were similar (see footnote *a* of table 5), as contrasted with the amounts of pentosans, it is very probable that the additional volatile material arose from the cellulose in the samples. On the other hand, it is extremely improbable that the fractions referred to represent pentosans, since that would require that the pentosan content of each material, regardless of its orginal value, should reach a common value, other than practically zero, after 300, 450, 600, etc., ml of distillate. Only in the case of the two pulps containing relatively large quantities of pentosans, samples *G* and *H*, does it appear that small quantities of pentosans, 0.2 percent, remain unconverted after 300 ml of distillate, and that even in these examples the fractions after II are essentially the same as the corresponding ones of the other pulps.

TABLE 5.—*Results of continued "simple" distillation with* HCl *of cellulose materials from cotton and wood*

[Expressed as percentage of pentosan [a]]

| Samples | I (initial values) | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| | Distillate fractions:[a] I to VII=300 ml | | | | | | |
| *A*, cotton [b, e] | 0.57 | 0.67 | 0.45 | 0.33 | 0.20 | 0.16 | 0.11 |
| *B*, new white rag (cotton) paper [b] | .66 | .68 | .49 | .34 | .20 | .19 | .12 |
| *C*, new white rag (cotton) paper [b] | .75 | .65 | .47 | .35 | .21 | .32 | .11 |
| | Distillate fractions:[a] I=300 ml; II to VII=150 ml | | | | | | |
| *D*, special sulfite pulp [d] | 1.33 | 0.46 | 0.46 | 0.38 | 0.33 | 0.25 | 0.06 |
| *E*, special sulfite pulp [d] | 2.86 | .44 | .42 | .40 | .32 | .14 | .09 |
| *F*, sulfite pulp | 4.72 | .44 | .39 | .33 | .25 | .19 | .16 |
| *G*, unbleached sulfate pulp [b] | 8.44 | .67 | .42 | .31 | .20 | .12 | .08 |
| *H*, soda pulp | 16.05 | .68 | .46 | .28 | .24 | .18 | .13 |

[a] The calculations were based upon the weights of the 1-g samples, corrected for moisture, ash, and resin, which thereby became as follows for samples *A* to *H*, respectively: 0.93, 0.83, 0.92, 0.96, 0.92, 0.91, 0.87 and 0.92 g. Paper samples *B* and *C* were made from the same batch of cotton rags. Paper *B* contained 10 percent of clay filler. The expression used for the claculations is given in the section "Method in Detail," omitting the constant *c* in these instances.

[b] These experiments were performed by C. I. Pope.

[c] This material was highest quality sterilized cotton, such as is ordinarily used for surgical purposes.

[d] These pulps had been subjected to modified chemical purifying processes by the manufacturers.

[e] The values for all fractions were corrected for the slight amount of volatile material arising from the rubber stoppers, which was found to be 0.02 percent per 150 ml of distillate, expressed as pentosans. This was found by distilling 300 ml of 12-percent hydrochloric acid alone in the apparatus.

The question now arises as to how much volatile material due to cellulose was obtained during the regular pentosan determinations in fraction I. This quantity could be estimated graphically from the values for the distillate fractions beyond I; or more simply, and sufficiently precisely for the present purpose, by selecting values which are compatible with those of the subsequent fractions. To do this, it is necessary to know something of the relative rates of evolution of volatile material by cellulose before and somewhat beyond the 300-ml point. That this rate is not greater before than after the 300-ml point is shown by the data for the cotton materials *A*, *B*, and *C*, in table 5, wherein the values for fractions I and II are essentially equal.

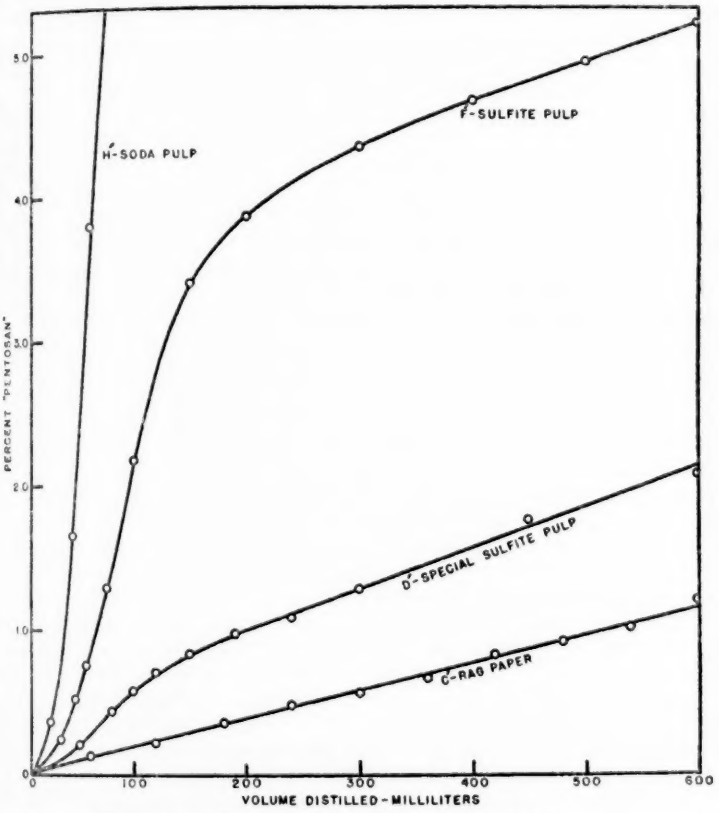


FIGURE 1.—*Rate of evolution of volatile material.*

A more detailed study of the "simple" distillation with sample *C* was made, again using a 1-g sample. The volatile material was determined in successive 60-ml fractions for the first 600 ml. The corresponding curve *C'* is shown in figure 1 and is best represented by a straight line. This shows definitely that the rate of evolution of volatile material from cellulose is not greater before than after the 300-ml point. A basis is thus established for assigning a maximum value of approximately 0.9 as the amount of volatile material due to

cellulose in the first distillates by the simple procedure, for samples *D*, *E*, and *F*. For samples *G* and *H* this value would be higher if only fraction II were considered. As previously mentioned, however, fraction II for samples *G* and *H* appears to be abnormally high because of small amounts of residual pentosans, since beyond II the distillate fractions for samples *G* and *H* resemble closely the corresponding fractions for samples *D*, *E*, and *F*. Thus, 0.9 appears to be the maximum value for all of these materials.

The maximum value of 0.9 is in good agreement with the minimum value of 0.8 previously arrived at in another manner. There is, however, evidence available that 0.9 is also a most probable value from the standpoint of the reasoning just employed. In the study of reaction rates in general, a straight line usually indicates that only one substance is reacting with the medium—in this case, hydrochloric acid. This is especially true where large differences in the amounts of two possibly reactive materials, polyoses and pentosans, are known to exist. By the method of redistillation of the distillate from sample *C*, table 3, shows that most of the original distillate was not furfural. Even if it could be shown that the small amount of stable volatile material in the third redistillation of sample *C*, table 3, were furfural, there still remains the possibility that such a small amount of furfural could arise from the decomposition of hydroxymethylfurfural, as several workers report.[15] Thus, the most probable assumption is that curve *C'* is due to cellulose, and that the rate of evolution of volatile material by cellulose is essentially equal before and somewhat beyond the 300-ml point. This assumption does not rule out less probable possibilities, but furnishes a measure of substantiation of the value of the correction 0.9, already fixed by limits.

The correction 0.9 refers to the cellulose in the fibrous materials studied, and is apparently not affected by wide differences in the small amounts of other materials present, such as resin,[16] lignin, wax, etc., known to exist in these types of pulps. Furthermore, the cellulose itself had been subjected to widely different treatments in the normal preparation of these pulps, without affecting this behavior of the cellulose. Since, moreover, the pulps studied were representative of the usual papermaking materials, it appears that the correction is generally applicable to like distillations of such commercial materials.

It was deemed of interest to continue the detailed rate studies of the other pulps listed in table 5. An entirely different type of curve was obtained with the special sulfite pulp *D*. For the first 180 ml, curve *D'* resembles in type curves *F'* and *H'*,[17] especially in that the maximum rate, corresponding to the maximum slope, appears at about the same part, 75 ml, of all three curves, which apparently is characteristic of pentosans. From 180 to 600 ml, curve *D'* is very

[15] Kirnmayer, Chem.-Ztg. **19**, 1003 (1895). Erdmann, Ber deut. chem. Ges. **43**, 2391 (1910).

[16] Glue, starch, and casein, often present in papers, were found to give rise to volatile material not exceeding 0.04 percent, calculated as a pentosan. This was determined by distilling quantities of these materials corresponding to the high glue, starch, or casein contents of 4 percent, based upon the weight of the paper, alone with hydrochloric acid as usual and then analyzing with bromate-bromide, etc., by the usual method.

[17] The remainder of curve *H'* was omitted for convenience. It can be reconstructed, if desired, from the following rate data for curve *H'*:

| Volume distilled: | *Pentosan* | Volume distilled—Continued. | *Pentosan* |
|---|---|---|---|
| *ml* | % | *ml* | % |
| 20 | 0.36 | 150 | 12.49 |
| 40 | 1.65 | 180 | 14.25 |
| 60 | 3.80 | 220 | 15.09 |
| 80 | 6.10 | 320 | 15.94 |
| 100 | 8.74 | 420 | 16.39 |
| 120 | 10.65 | 520 | 16.74 |

similar to $C'$, and in this region the volatile material in both cases apparently arose from cellulose. The slope of the latter part of $D'$ is 1.6 times that of $C'$, which probably represents the difference in the rates of hydrolysis of the two types of cellulose. If it may be assumed that the cellulose in cotton is more resistant to hydrolysis than that in wood pulps, under the conditions of distillation, as it has been found to be in highly concentrated, 41-percent hydrochloric acid,[18] it is seen that hydrolysis, or another similar reaction, is a necessary preliminary step in the production of volatile material from cellulose. Finally, it is seen from figure 1 that the slope of the straight portion of curve $F'$ is the same as that of $D'$, which is to be expected if the same type of cellulose is here producing the volatile material.

The straight line, occurring before the 600-ml point is reached, appears to be characteristic of cellulose, and is the type of curve to be expected as long as the available reactive surface does not change appreciably in area. Beyond 600 ml. the reactive area apparently diminishes rapidly as the fibers start to distintegrate and disappear, after which the rates of production of glucose, and consequently of the volatile material, decrease, and the curve approaches a limiting value.

Small amounts of methylfurfural are probably also obtained from the methylpentosans during the regular determination. This may be distinguished from furfural, when these two are present alone,[19] but in distillates from cellulose materials the presence of hydroxymethylfurfural makes the direct application of the method uncertain. This does not matter for the present purpose, since the method is intended for the determination of pentosans as a group, as distinguished from cellulose.

## III. METHOD IN DETAIL

In view of the results obtained in this study, the following method is recommended for the determination of the pentosan content of pulps and papers.

Approximately 1 g of the ground material is taken for analysis. The distillation is performed in a 500-ml distilling flask, above which is mounted a separatory funnel containing 400 ml of 12-percent hydrochloric acid. Rubber stoppers may be used if desired. One hundred milliliters of the acid is added to the sample from the separatory funnel and the remaining 300 ml is added dropwise as rapidly as necessary to maintain the volume in the distilling flask at 100 ml. A water-cooled condenser delivers through an adapter into a 1-liter glass-stoppered reagent bottle. The time of distillation is 100 minutes, during which time 300 ml is distilled. It is important to observe the requirements of time and quantity.

Fifty milliliters of water and approximately 250 g of crushed ice [20] are added to the distillate. After the temperature has fallen to $-2°$ to 0° C, 20.00 ml of 0.2 $N$ bromate-bromide solution [21] is introduced with a minimum of agitation, after which the reagent bottle is closed and shaken well. After 5 minutes, 10 ml of a 10-percent solution of

[18] E. C. Sherrard and A. W. Froehlke, J. Am. Chem. Soc. **45**, 1729 (1923).
[19] Elizabeth E. Hughes and S. F. Acree, Ind. Eng. Chem., Anal. Ed. **9**, 318 (1937).
[20] The ice should be relatively pure, although this is not essential, as some of the same ice is used in the blank determinations.
[21] Contains 5.57 g of $KBrO_3$ and 50 g of KBr, both of reagent grade, per liter.

potassium iodide is added. After again shaking the bottle thoroughly to allow absorption of the bromine vapors, the free iodine is titrated with 0.1 *N* sodium thiosulfate solution, using starch indicator.

The blank is determined by diluting 270 ml of 12-percent (3.5 *N*) hydrochloric acid to a volume of 350 ml, adding ice, bromate-bromide, and potassium iodide in the usual manner, and titrating with 0.1 *N* thiosulfate solution.

The pentosan content of wood pulps and papers made from wood pulps is calculated by substitution in the following expression:

$$\text{Pentosans, percent} = 1.03\left[\frac{6.60 \times N \times (v_2 - v_1)}{W}\right] - C$$

$C$ = volatile material arising from cellulose during the simple distillation. It has the value 0.9 for 300 ml of distillate.
$N$ = normality of thiosulfate solution.
$v_2$ = blank on bromate-bromide solution under test conditions.
$v_1$ = volume of thiosulfate solution necessary to titrate the solution after oxidation.
$W$ = weight of the test specimen after correcting for moisture, ash, resin, glue, and starch.

The factor of 1.03 is the correction necessary to account for the loss of furfural during the distillation from a pulp. This loss was taken as approximately 3 percent, based upon the average loss occurring in distillations of the usual amounts of furfural.

The factor 6.60 is the product of $100 \times 0.0480 \div 0.727$, in which 0.0480 is the weight of furfural in grams corresponding to 1 ml of *N* thiosulfate solution, and 0.727 is the theoretical conversion factor of pentosans to furfural. If the analyst desires values which are comparable with those used in Kröber's tables, in which the conversion of pentosans to furfural is arbitrarily assumed to be 80 percent, for which the conversion factor is 0.582, the following expression may be used, disregarding the furfural and the cellulose corrections:

$$\text{Pentosan content, percent} = \frac{8.25 \times N \times (v_2 - v_1)}{W}$$

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